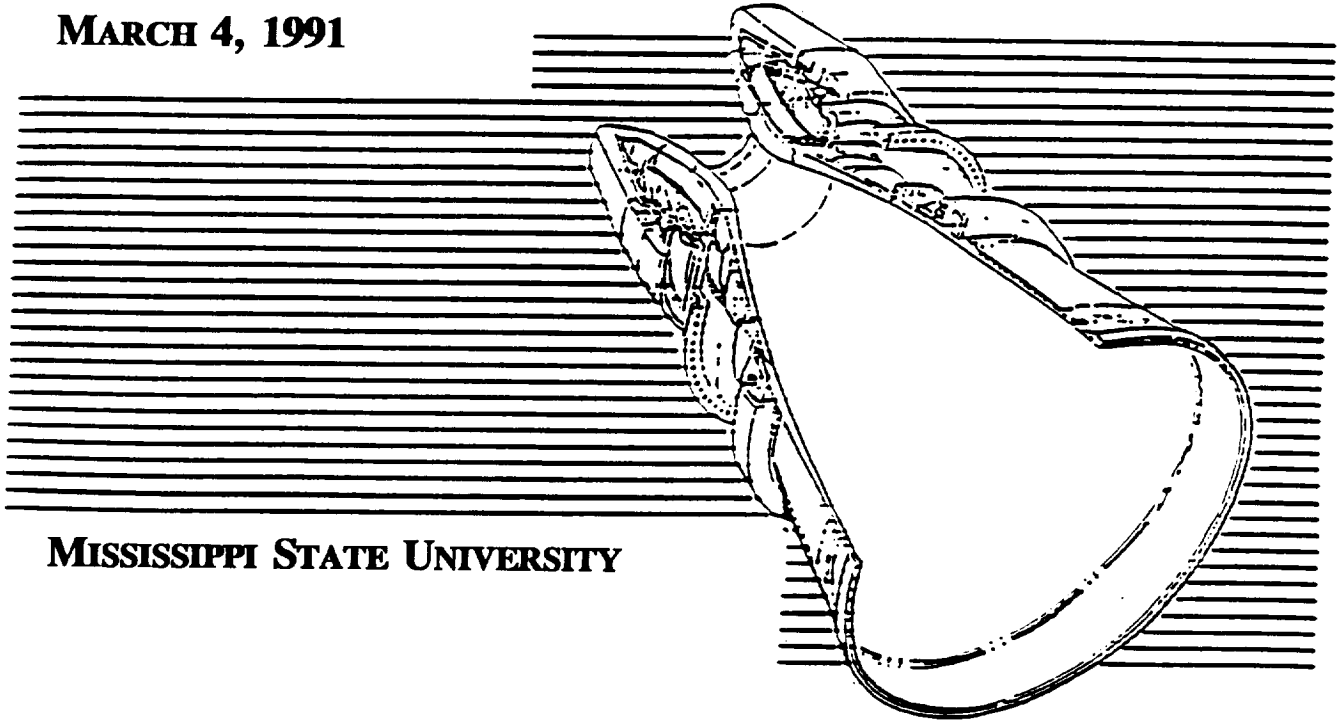


**PROCEEDINGS
ADVISORY COMMITTEE
ON STANDARDIZATION OF CARBON - PHENOLIC TEST
METHODS AND SPECIFICATIONS
ELIZABETHTON, TENNESSEE
NOVEMBER 15 - 16, 1990**

MARCH 4, 1991



MISSISSIPPI STATE UNIVERSITY



NASA GRANT NAG8-545

ATTENDEES

INDUSTRY ADVISORY COMMITTEE ON CARBON-PHENOLIC TEST METHODS AND SPECIFICATIONS

**NORTH AMERICAN RAYON CORPORATION
ELIZABETHTON, TENNESSEE
NOVEMBER 15-16, 1990**

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**SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE
ON STANDARDIZATION OF CARBON-PHENOLIC
CONSTITUENT TEST METHODOLOGY**

**NORTH AMERICAN RAYON CORPORATION
ELIZABETHTON, TENNESSEE**

AGENDA

THURSDAY, NOVEMBER 15, 1990

8:00 AM - 8:30 AM	Committee Preparation
8:30 AM - 9:00 AM	Welcome by Charles K. Green, President and CEO of North American Rayon Corporation
9:00 AM - 9:15 AM	Introduction by Committee Chairman, Bill Hall, Mississippi State University
9:15 AM - 10:00 AM	Advisement Task 6, Ashing Procedure and Alkalai Metal Content of Carbon Fiber and Fabrics <ul style="list-style-type: none">● Ismail Ismail, Dayton University/AFAL
10:00 AM - 10:30 AM	SPIP Product Identification Code <ul style="list-style-type: none">● Pat Pinoli, LPARL● Jack Williamson, Consultant
10:30 AM - 11:00 AM	SPIP Initiative to Adopt a Water-Soluble Rayon Yarn Lubricant/Size for Weaving <ul style="list-style-type: none">● Tom Paral, Polycarbon
11:00 AM - 11:30 AM	Advisement Task 2, Fabric Oxidation Mass Loss Test <ul style="list-style-type: none">● Myles Towne, AMOCO● Pat Pinoli, LPARL
11:30 AM - 12:00 N	Shelf Life Limit for Prepregs, Industry Standard <ul style="list-style-type: none">● Ed Mills, CSD
12:00 N - 1:00 PM	Lunch
1:00 PM - 1:30 PM	Silicone Contamination Update <ul style="list-style-type: none">● Tom Bhe, Aerojet
1:30 PM - 2:30 PM	Advisement Task 1, Resin, Filler and Fabric Content in Prepreg <ul style="list-style-type: none">● Peter Kraus, The Expert Systems Technology, Inc.● Ed Hemmelman, Fiberite● Bill Armour, Aerojet
2:30 PM - 3:15 PM	Advisement Task 4, Carbon Assay Testing Calibration <ul style="list-style-type: none">● Cindy Upton, NASA/MSFC● Tom Paral, Polycarbon● Gene Rubin, Hitco

**SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE
ON STANDARDIZATION OF CARBON-PHENOLIC
CONSTITUENT TEST METHODOLOGY**

**NORTH AMERICAN RAYON CORPORATION
ELIZABETHTON, TENNESSEE**

**AGENDA
THURSDAY, NOVEMBER 15, 1990 (CONTINUED)**

- | | |
|-------------------|--|
| 3:15 PM - 4:00 PM | Advisement Task 5, NASA/Thiokol Rayon Specifications <ul style="list-style-type: none">● Rick Golde, Thiokol● Bill Hall, NASA/MSFC |
| 4:00 PM - 4:15 PM | Rapier Loom Selvage Edge Experience <ul style="list-style-type: none">● Wayne Johnson, Highlands● Don Beckley, BP/Hitco |
| 4:15 PM - 4:30 PM | NASA/AF Alternative Source Qualification Program for Rayon <ul style="list-style-type: none">● Ben Neighbors, NASA/MSFC● Ken Drake, Aerospace● Ed Mills, CSD |
| 4:30 PM - 5:00 PM | SPIP Low Conductivity PAN Program <ul style="list-style-type: none">● Pat Pinoli, LPARL● Rick Golde, Thiokol |

**AGENDA
FRIDAY, NOVEMBER 16, 1990**

- | | |
|---------------------|--|
| 8:30 AM - 9:00 AM | Executive Review of Action Items from Thursday Meeting |
| 9:00 AM - 10:00 AM | Tour of NARC Manufacturing Facility |
| 10:00 AM - 11:00 AM | Tour and Review of Testing Methodology |
| 11:00 AM - 12:00 N | Open Discussion by Committee on Rayon Acceptance Test Requirements |

THE INDUSTRY ADVISORY COMMITTEE

FOR

CARBON-PHENOLIC CONSTITUENT TEST METHODOLOGY

IS

CONSTITUTED UNDER PROJECT 3:2.1.1

OF THE

SOLID PROPULSION INTEGRITY PROGRAM

(SPIP)

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Hall We are ready to get started. Our host for this meeting is North American Rayon and our contact was Bob Looney from North American Rayon and Bob will start the program off with an introduction of the welcoming group.

Looney Before I introduce the people from North American who will give the official welcome to you—a few housekeeping chores. We do have fax facilities, we have copying facilities here. If we need major copies, we'll get those done over at the plant. We are not that far away and we can easily shuttle it and have it back within an hour. When we get through the day's proceedings after all the papers have been presented, if copies are needed, just let me know and we'll get them to you either late today or tomorrow morning when you visit the plant. The schedule for tomorrow is on your agenda and we are looking forward to having you at the plant but tonight we are going to have dinner at the House of Ribs Restaurant here in Johnson City and we'll give you directions to that. Dinner is scheduled at 6:30. I assume most of you have transportation, either cars that you have rented, but if any one needs a ride, those of us who live here can easily come by and pick you up at the hotel. Is there anyone without transportation? We are here to please and to serve. If there are any other things that you need, we will try to provide it. You just have to let me know and I will be your contact for whatever services you need, either from the hotel or from the plant. At this time I would like to introduce to you the Director of Marketing for North American Rayon, Dick Reagan and he will be followed by the Vice President of Manufacturing, Allan Snodgrass.

Reagan Good morning, ladies and gentlemen. Welcome to the Tri-Cities. Thank you for the weather you brought with you. I understand it is going to be up in the seventies today and tomorrow and plenty of sunshine, just like California weather. On behalf of the employee-owners of North American Rayon Corporation, I would like to welcome you to the Tri-Cities and to our facilities over about 7 miles from here in Elizabethton which you will be seeing tomorrow. Charles Green, our President, had planned to be here this morning to welcome you but he ran into a problem this past week on the treadmill test. He found out that he has a blockage in one of the arteries going to his heart. He is going to have surgery tomorrow down in Birmingham to correct this situation. It is not a serious situation, according to his doctor, but I think anytime you have an operation on your heart, it is serious. But he plans to be away from the office for a few weeks and I would say that probably by the first of the year, he should be back in the shop with business as usual. If there is anything that anyone has on their mind concerning the company, please feel free to call myself, Allan Snodgrass, Bob or any of us that would certainly help you with whatever you need. Allan is going to talk a little bit about our plant situation. I would just like to mention briefly about our business. Our business, as most of you know, North American Rayon is primarily rayon, filament yarns, textile yarns, industrial yarns, pre-cursor yarns, as you know for the carbonizable product, rayon tow and we also

have a polyester staple plant over next to our rayon plant. Our business is good. We have been extremely fortunate to be in the end of the business that, especially in the apparel end of the business in women's wear, mainly, where we manufacture high-priced yarns for high-priced dresses, blouses and skirts for women and some men's wear. Our business continues to be good mainly because women are continuing to buy these really attractive rayon dresses. We don't see that coming to an end anytime soon. We are very happy, we are making money, we have been profitable for the last five years, and we expect to remain that way. Our industrial end of the business where we sell heavy denier yarns into the tire cord area, into rubber reinforcing products. That business is not good, mainly due to a fall-off in the automotive market. Most of you are familiar with the problems the automotive people are having selling domestic cars. We are tied right into the automotive business, but that business is not good. It hasn't been good for about six months. However, the other sectors of our business are very good, in fact we have been on allocation for textile yarns for the last three years. We remain that way. On the precursor yarn, Allan will talk a little bit about what we are doing there. We have been in this business a little over a year and we think it is a business worth pursuing and we continue to do that. Again, I hope all of you have a very good meeting here this morning and tomorrow. We hope that you will enjoy your visit to the area. Thank you.

Snodgrass

Let me just re-emphasize something that has already been said. We welcome you to the Tri-Cities area. The weather, I don't believe anybody can request any better weather than has been forecasted for the next two or three days. You are really getting to see the edge of the mountains and its color. We do want to welcome to North American and we will wait until in the morning to show you the facilities. We have about 32 acres under roof and along with our other 1500 employee-owners, we will try to answer any questions you have as far as our production capability. Just to mention one thing, we did have some little trees since rayon is a renewable resource. The little tree, you are welcome to have one of those and it goes into a little background on rayon and the little velvet bag is also 100% rayon so there's plenty up here on the table and if there is not enough here there are plenty more that Bob has outside, so if you would sometime today, help yourself to one of the bags. If there is anything we can do to make your visit to East Tennessee more enjoyable or any more productive, all you need to do is holler at Bob and we will do whatever we can. We look forward to having you at the plant tomorrow and I know you have a full agenda today. We just wanted to take a minute or two to welcome you to Upper East Tennessee and tell you that we are proud to be hosting the meeting and we look forward to having you at the plant tomorrow. If there is anything we can do to make your visit any more fruitful, just holler at us. Thank you and we look forward to seeing you tomorrow.

Hall

Thank you. I would like to spend just a few seconds to reinforce the reasons why we are here. We are part of the Solid Propulsion Integrity Program that is funded out of Marshall with Hercules as the prime contractor. The overall objective in the SPIP program is simply to improve our data base, knowledge and our techniques so that we can improve the solid propulsion industry as we go through the evaluation of the various nozzles and new materials. That is the overall SPIP objective and our committee happens to be one task of many in the SPIP program and is established under the 3.2 Task Area and we are charged with look into the test methodology and specifications. This comes about because when this program was initiated, it was found that there was quite a bit of variation in test methods utilized in the industry and that there were specifications that were not quite what they should be. We have been evaluating for three or four years, the various test methods and the specification limits of the materials that are used in the prepregging of constituents of the solid rocket motors. Two criteria are used. First, the question is asked, "Does the test method actually yield the desired results, does it actually measure what you are trying to measure? Does the number you get relate to the true value?" We do this mainly by round robins. We have various labs run the same test and we correlate between labs. Once we satisfy this question that we really do have a good test method that can be reproduced from one lab to another, then we are happy with the test method. Then we answer a second question, "Does this value that we obtain, does it really have any true meaning as far as the usefulness of the material. Now we have eliminated test methods and we have eliminated specifications because they don't meet both of these requirements. There is no need to run a test, no matter how accurate it is, unless it gives you information that you can use. This is the way this committee operates. It is an industrial advisory committee and we really appreciate the support that we get from industry. That is basically it. Does anybody have any questions? Most of you are oldtimers at this. We do have a lot of Air Force participation this time that we have not had in the past, and I would like to thank you for this. We are very appreciative of that. I might mention that we have the NASA representatives with us this time, which both of them are new to this committee. We have first, Kim Turner, who is the advanced solid rocket motor contact at Marshall and then we have Cindy Upton, who is this committee's contact at Marshall and you will all receive an attendance sheet with all of our names, phone numbers and companies.

Pinoli

A couple of comments. If there is anything that you would like to include in the minutes of the meeting, please pass them on to Bill and he will make sure that they get into the report, either as an addendum or as part of your presentation. I find this to be an excellent method of keeping track of the work that we are doing. Otherwise you end up with an office that looks like my own. Data is really a resource. In fact just recently, I was looking back at some of the work that we have done on oxidation behavior and the only place that I could find it was in the report. The other thing

that I would like to make a comment about is the Twentieth Biannual Conference on Carbons that is going to be held at the University of California, June 23 - 28, 1991 and I encourage everyone here to participate in the conference. Dr. Ismail and I have handouts for those who would like to attend and submit a paper. We expect attendance to be around 500 or 600 people from around the world. It is truly international in scope and if you have an interest in carbon you will enjoy one week at the University to be reindoctrinated in the academic world and the people who are at the leading edge of carbon research. Those that have been in a carbon conference before, I expect to see there again. Another thing that I would like to make a comment on is with regard to the operation of this committee. It is very informal, feel free to get up, grab a cup of coffee, walk around the room. We try to maintain very little formality. We are not here to criticize, we are here to help everybody. You are going to see data that's being conducted by manufacturers amongst themselves and the last thing that we want to do at a meeting of this nature is to criticize anybody. The intent of the round robin testing is to get a handle on the confidence level in the data that is being generated. If we can't develop confidence on test methodology, we are just fooling ourselves from the engineering standpoint in trying to make very strong and costly decisions. It is very important that we understand the test accuracy and precision of work that is being performed within our industry. With that, Ismail, is going to lead off with a subject we have had under advisement for some time.

Ismail

Today we will discuss several aspects, but I can group them into three main titles, oxidation rates of fibers and fabrics, high temperature ashing, and low temperature ashing. By low temperature ashing, I mean oxidizing the fibers or fabric with atomic oxygen. I will be wrapping up my talk with some simple conclusions and simple recommendations. In my introductory part, I will be addressing why it is important to determine the sodium and alkalis. They are good catalysts for any reaction between carbon and other reactive gases.

I started this business because Pat Pinoli kept challenging me for about 6 years about STS8A and B nozzles. He said, "We have one of them giving excessive erosion and the other one giving nominal. The fabric used here is this, and the fabric used here is that. Can you help?" He stopped there and of course he expected the help in the area where I am active, like oxidation rates or some structural properties like surface area and porosity. Of course by finding some of the reasons does not mean that these are all the reasons for excessive erosion. But some of these properties are affecting the erosion of the nozzle. I started measuring oxidation rates under certain conditions and found that the fabric oxidizes at much faster rate than the other. I checked the sodium and ash and certainly the first fabric had higher levels of sodium and potassium than the other one. Then we found that all fabrics gave lots of gases and have a considerably high level of microporosity properties. But in today's

presentation, I'll be concentrating more on the sodium and potassium levels as well as oxidation rates.

Now the first question to ask is whether sodium really catalyzes different reactions of carbon fabrics in different ways. We prepared a mixture simulating rocket nozzle exhaust; it had CO, CO₂, hydrogen, nitrogen and moisture. We see the net effect of reaction between fiber and this mixture of gases, dry or wet. The solid lines are for mixture B (dry) and the dotted lines are for mixture A (wet). No matter which mixture we use and regardless of the temperature, we still see that the material with a higher level of sodium and potassium (CSA-4671) is going faster than the material that has lower levels (CCA-3K15D).

Then we looked at oxidation rates and I am putting here the same two materials compared to some other materials. The oxidation of any carbonaceous material depends on at least five factors: (1) the active surface area, (2) presence of porosity in the fiber, (3) extent of development of porosity in the fiber during gasification, (4) presence of impurities (sodium, potassium, calcium and other impurities) which catalyze the reaction, and (5) how the fabric weaved. I think the way by which the fiber is weaved does have a tremendous effect on oxidation rates.

Figure 2 illustrates the oxidation rates of five different samples: VSB 32 (a graphitized pitch fiber), WCA, T300 (carbonized PAN fiber), CCA-3K15D and CSA-4671. The first three materials do not have high levels of sodium and potassium. We can rule out the issue of catalytic effect. The T-300 did not see high temperature like the other two and what we see here is a structural effect. If the fiber is heat treated at low temperature, T-300, the oxidation rate is faster. If the fiber is heated to higher temperature, the structure closes. The crystallites grow together, and the porosity is lost. The heat treatment aligns the crystallites more and more, and decreases the concentration of active sites. T-300 has a higher ASA than the other two. As we move to the case of CSA and CCA-3 in Figure 2, we find that we are changing the structure and enhancing the sodium level. The two fabrics have a considerable level of microporosity but the CSA-4671 has a much higher level of sodium than the CCA-3K15D. Therefore, the difference in their oxidation rates is attributed to the catalytic effect of sodium.

Armour

I was just wondering how reproducible that data is and how many data points you have on there.

Ismail

On each one of these plots we have about 3000 data points.

Armour

What is the spread? Is that an average?

Ismail We are looking at the average of 3 runs on each fabric, and of 15 runs for the fibers because these were carefully executed for some other project. I am very confident with the data. I may add that the samples were heated to 1000°C, then cooled it to 500°C. Air was then injected at the given flow rate of 100 cc/min.

DiMeo You said that weaving had a big effect on, could you briefly describe the effect of weaving.

Pinoli Ismail, where are you coming from on the issue of weaving?

Ismail I cannot tell you much about this simply because I don't have enough data. When we talk about weaving a fiber, we then talk about the accessibility of gases to internal surfaces. In other words, think of it in one extreme, you have a bundle of separate filaments hanging loose in air. Most of the surfaces will be exposed to air. In the other extreme, think that you are weaving it tighter in a certain way, therefore, some of the surface will not be exposed to oxygen because it will be hidden underneath the other filaments, and it will not see oxygen. In the former case, the fiber will oxidize faster. At the other extreme we only oxidize the top (outer) portion of the fiber without getting oxygen molecules into it. So we don't get consistent oxidation in the second case. Is this explanation good enough for the time being?

Pinoli No. Go a little bit further. Have you looked for cementation or any other indication that you have carbon deposits on the fabric surface?

Ismail Do you mean SCM?

Pinoli Yes.

Ismail Let's move to the next two slides, Tables 2 and 3. Here the fibers I am covering in today's presentation were not made in one time frame period. They were covering a period of three or four years. I did include here fifteen different WCA fabrics. I got them at random from all over the country. I just called people and asked them to send me some of their WCA and to tell me anything about it. Some of them did, and some of them couldn't. Special emphasis here is given to Sample #6 which had discoloration bands. When they store these on the shelf, the fabrics start showing gray and black areas, and nobody knew why. I was trying with this particular sample to see whether the gray area was different than the black area, or whether all areas were the same. They turned out to be the same, at least with the kind of test I was doing. I got Sample #9 from friends in NASA and they said, "It is bad, it is very bad!!" I didn't see anything bad in terms of sodium or potassium or other surface properties, but it probably has bad mechanical properties. I got Sample #18

from Pat in 1986. This is the standard fabric I am using for the rest of my work on CVD and CVI. It is probably the best one I have characterized. Sample #19 comes with a very special story. About 4 or 5 years ago, in a JANNAF meeting, someone said that there was a lot of silicon on WCA fabrics. They claimed that the manufacturers were putting a lot of silicon on fabrics, coming from the pump or something else. Of course when some new story comes in, we get some believers, we get some disappointed, and we get some guys like me who are puzzled by a new phenomenon. I think I was a little bit more curious to check whether this particular fabric has such high levels of silicon or not. That is why I worked on it. Samples #20 and #21 are the ones used in STS8A and B.

Samples 22-30 are the low fired rayon fabrics. We were looking at low fired rayon fabrics coming from Hitco or Polycarbon or Amoco (Union Carbide). Samples #23-#25 were manufactured by Hitco, roll #1 had a high level of sodium. Roll 2 had a medium level, and roll #3 had a lower level of sodium.

Figure 3 shows the low temperature ashing. We have an evacuated chamber with the fiber samples inside. We then inject some oxygen into the system, still under a vacuum, with a maximum pressure something of 2 or 3 torr. We then we apply a radio frequency power, anywhere from 20 to 300 watts, and the power ionizes the oxygen molecules to give oxygen atoms. In addition, we get different kinds of ions. They all start attacking the sample because carbon can react with atomic oxygen, or with the ions, at room temperature or slightly higher. Therefore, the ash cannot evaporate. The parameters that we change while ashing the sample, which affect the rate of ashing, are: (1) how much oxygen we put in, which means also the pressure inside the chamber (the higher the flow rate, the higher would be the pressure), (2) how much pressure we have to ionize O_2 . Generally there are two main reactions. One is carbon sputtering (O_2 hits the surface and some gets out), and chemical etching (reaction between carbon and oxygen atoms). If we are operating at very low pressure flow rate of oxygen, we mainly get sputtering. If we increase the pressure, we get chemical etching.

Pinoli Was this the technique you used for all of your ashing experiments?

Ismail No, no. I used high temperature. This is a new technique that I am introducing. I feel a lot more comfortable with it than high temperature ashing.

Table 4 summarizes some of the ASTM ashing procedures. According to the book I used, the ASTM book (of 1985), there is no standard procedure for carbon fibers/fabrics. I was surprised. They have procedures for carbon blacks, activated carbon, graphite, coal and coke, petroleum coke and graphite lubricants. Let's compare and see how well we compare to the ASTM. The third column tells you

the starting weight of the sample. It is either 2 grams or you pick up your choice. We keep ashing until we get sufficient 0.1 grams ash!! As we can see, there is no specific guidelines for the starting weight of the sample. In terms of temperature, they tell you what they recommend but if you don't get complete ashing, go for longer times. The first procedure says to start at 550, the oven should be preheated, and do it for 16 hours uncovered. If we see carbon black, go to 950 for 4 or 5 hours and it is permissible. After all, here is your repeatability if you are doing it over and over ($\pm 20\%$) and here is your reproducibility (23%). If I do it in my lab and Pat does it in his lab and we are $\pm 23\%$ off, we are okay. Of course it doesn't make sense to me, but this is what they say. If you have activated carbon use a preheated oven at a 650°C higher temperature. I don't understand why for the carbon blacks, it is 650 and here, for activated carbons, it is 550-although the activated carbons are one order of magnitude more active than the carbon blacks. I would go the other way around but this is how they listed it. For graphite you, heat it gradually at 500°C for 1 hour, 750°C for another hour, then 950°C in 1 hour and use a platinum dish. For coal and coke, we go to 450-550°C and for 1 hour, then to 700-750°C for 2 hours or more. We can see from the table that any temperature could be okay as long as it is between 500 and 950°C. The repeatability (8th column), I don't know why it is still being investigated until now for activated carbons and being developed for graphite. I don't know what took them so long since 1969. They are still developing some checkoff. I could do it in one week. This is what they put in the 1985 book. As you can see, you can do anything with the ashing and you could come back and say it is an ASTM procedure.

When we ash a fiber or fabric, we have several possibilities. Either the temperature is low and the time is short, or we have a high temperature and long time (the ASTM doesn't give you much about time). The lowest temperature they say is 550°C and the highest is 950°C. The shortest time they mentioned in the book is 1 hour and the longest is to keep ashing until we get a constant weight or until all of the carbon is burned out. Of course with each step, we have the possible result of incomplete ashing if we are too low on everything. If we are too high on everything, the ash may evaporate. Thus, we either overestimate or underestimate the results of ash; depending on the material you have in question.

Well here is my first conclusion. (Figure 4) We are talking about two WCA fabrics heated gradually to 750 and heated to 950 and we got zero ash. I am the one who did this particular test. My conclusion right away is not to ash at 950°C. But really when I ran this test that was not my objective. I don't have time to waste on ashing materials like this. The reason for ashing these two particular WCA fabrics was to check for silica. I was using the same samples that people were claiming to have higher levels of silicon. As you can see here, if we ash to 950°C we end up with zero ash. If we have silicon there, it is not going to escape at 950°C. But if

everything escapes at 950°C, we definitely have something else but silicon. That was one of the main reasons for running this test. You noticed that I was using much higher starting sample weights. I was checking two things with the same run: (1) how reproducible I could be if I put two different samples under the same conditions, and (2) how consistent the samples were. What you see here in Figure 4 is the difference between 400 and 600 ppm. I am concluding that with WCA materials, if our ppm data agree within 50% of someone else, we are probably okay, simply because the material is not consistent as we analyze it. You might take a portion here from one end and get a certain sodium. You might take a another portion at the other end and get a different value. The difference could be as high as 50%.

Pinoli Myles, are those numbers reasonable for parts per million of ash in a WCA fabric?

Ismail No. Did I say they were reasonable?

Towne On sodium?

Pinoli No, this is ash as presented in ppm.

Ismail This is ash, total ash.

Towne A tenth of a percent.

Ismail I am coming to that Pat. The values in Figure 4 could be right or wrong, so we do it again, but this time we lower the temperature at 750°C. (Figure 5) We heat to 750 and we hold there for three hours. We still see black spots, then we heated it longer at 750°C. We find that the ash is going down and we still see carbon spots. The question is, the longer you leave the ash with that little carbon spot, the more sodium will evaporate. Therefore we lose more ash to get rid of the remaining carbon spot. We have to make up our minds when to stop the run or how to steer it, so that we don't heat it forever to get rid of the carbon spot. There is always that trade-off between burning of the last carbon spot and how much ash we get at the end of the run.

Denault This is just in a Muffle furnace?

Ismail Perfect.

Hemmelman How did you ash those samples? How were the sodium levels determined?

Ismail By atomic absorption.

Hemmelman You had to ash the samples?

Ismail Yes. It's the same procedure. You have to ash the sample, but at lower temperature. Is this your question?

Hemmelman You don't think that the ashing temperature had any influence on the sodium levels that you obtained?

Ismail Not at 600°. If you ash at 750, yes it does.

Table 5 summarizes the results on all WCA fabrics; the low ash is 0.01 and the high ash is 0.09 percent. This is the different levels of sodium, anywhere from 0.1 to 12 ppm. I am putting here oxidations rates at 700°C and you can see that the rate of oxidation of all the WCA samples is more or less the same within 50%. No I think it is even less, I think, within 25%. The highest is 3.34, and the lowest is 2.69.

In Figure 6 we are showing some effect of temperature on the ash content. I am comparing it with the low temperature ashing I described a little earlier. The low temperature ashing gives a more realistic number. The high temperature ashing could be very close to it if we operate at lower temperature. You could see here that by ashing at 500°C, we are pretty good in agreement with the low temperature ashing, whereas when we go to 625°C, it starts going down. When we go to 750°C, this number drops to something like 0.3. Really with the material that has high sodium level, you don't want to go too high in temperature when you ash the sample. That percent of ash depends on how long you heat it. In Table 6, WCA-15 (C) has been heated overnight at 750, and (D) has been heated over the weekend at the same temperature, 750. Certainly 750 is not recommended for WCA. Here is another WCA material, WCA-14. This is my standard material, and I did ash it at 650°C. I would say there is good agreement between ashing at 650°C and low temperature ashing. We don't want to exceed the 650°C in ashing the graphitized fabrics like WCA.

In Figure 6 we see the effect of ashing temperature on materials. CSA-4671 is the fabric that is similar to STS8A. The other fabric was obtained from Polycarbon, it has really high levels of sodium, about 2900-3000 parts per million. I am showing here is the limit of high temperature ashing and the effect of temperature on how much ash we get. I would say that at 500-700°C, this is probably okay because we are losing some of the ash. but with it we are not changing the form of sodium a lot. When we lose ash, we could be decomposing some of the salts, or converting them to different kinds of salts without losing sodium. There are many chemical reactions taking place in this temperature range and take place even here without losing sodium. It is a very hard subject to say whether we are getting a salt decomposition

without evaporation or evaporation with salt decomposition. Clearly, if we exceed 700°C, we go far down in losing ash. If we go to the low temperature ashing, we are probably getting the highest possible number, and probably the most accurate one.

Table 7 summarizes all the data I got. We are talking about low fired rayon. They could have sodium anywhere from 2 ppm up to 3100 ppm. In the last two columns I am just normalizing the data.

In Table 8 we start washing the fabric itself. First we determined the sodium of the total fabric, and it is about 3100 ppm. We then took the fabric and washed it with double distilled water. We kept the filtrate and the fabric and we analyzed for sodium and potassium in the filtrate and in the fabric. We added them together. We can see that as we wash the fabric, we remove some of its sodium in the filtrate, but still retain some of the sodium with the fabric. The same is true for potassium. We did it with HCl and instead of washing with double distilled water, we soaked the sample in 1 normal HCl. The filtrate has more sodium which means that HCl removed more sodium from the fabric than double distilled water. Of course, the fabric retained less sodium; about 50%. On the other hand washing with double distilled water did not remove as much of the potassium as did the wash with HCl. This means that the potassium is present as a salt, and when we wash with water, it is removed. Potassium is also chemically bonded to the fabric. When we wash with acid, the chemically bonded potassium, in addition to the salts, is removed.

Pinoli

What is your explanation for your effectiveness of HCl in removing the sodium from carbon fabric?

Ismail

It is coming in the next slide. We have three different kinds of sodium in the fabric: (1) sodium as sodium salt on the external surface. You wash it, you remove it; (2) sodium chemically bonded to function groups on the surface, at the external surface again. Let's say the surface has OH or COOH groups. You could have sodium in place of hydrogens. This is true, and I know that what I am saying is true. The chemically bonded sodium is removed by acid and cannot be removed by water. That is about 5% of the external surface. (3) The rest of the sodium is inside the fabric itself. I think it is trapped in the micropores because those fabrics turned out to have micropore width of about 10.5 to 11 angstrom, and that this width is enough to trap some sodium inside the micropore. Of course we were curious to determine what form of sodium was there, and we talked about this in JANNAF meetings. It turned out that a good majority of the sodium is present as sulfate. I would say the rest is present as carbonate.

Figure 8 shows how the presence of sodium affects oxidation rate at 500°C for 10-12 different materials. As we increase the sodium level up to 1000 ppm, we start seeing a catalytic affect of sodium. Of course, the oxidation rate shoots higher as the sodium content goes to 3000 ppm. The arrows point at the CSA-4671 samples: as received, right arrow, water washed; middle arrow, and HCl washed; left arrow. Thus, simple washing with water would save lots of trouble in terms of removing the sodium. It doesn't eliminate it, but it removes at least 50% of the sodium.

Pinoli Surface sodium is more important in influencing the oxidation rate than the sodium that is within the fiber. That sounds to me as if it is an accessibility problem.

Ismail Yes. Thank you. Next we consider Figures 9 and 10 which show some possible relations between what I have seen from thirty fibers and fabrics. As long as the ash content is in the neighborhood of 0.1%, it is very hard to get accurate numbers. By the way, you can still get good accuracy if you use 1 pound and ash it. As the ash goes above 0.1%, we start seeing some shooting in the curve. While Figure 9 shows the low region, Figure 10 shows the high regions; the whole, entire region.

These are all different fabrics that we used in the study here. We could see a very good straight line when the ash exceeds 0.15%. What does this straight line mean? Well, if you look at the slope of this line, the slope means how much sodium is in the ash. Well, can we get some physical meaning of this slope? Yes. Let's say the ash is sodium sulfate or the ash is sodium carbonate, how much is the percent of sodium in sodium carbonate and how much is it in sodium sulfate? Make another plot for sodium carbonate and a third one for sodium sulfate. If we assume that all the ash is sodium carbonate, and we get a higher straight line with a higher slope because the sodium in sodium carbonate is higher than the fabric line. If we do the same calculation for sodium sulfate, we get another lower straight line with a lower slope. Our line for the fabrics ash is in between. What it simply says, is they have a mixture sodium carbonate and sodium sulfate. I confirmed it by ion chromatography. We do have sulfate. Of course I didn't confirm it in all of them, but I did confirm on this one. I did it by a very old procedure. We know that barium sulfate is insoluble in water. We prepare the ash solution and mixed it with a known amount of barium (nitrate solution). If you have sodium sulfate, barium sulfate will precipitate and the concentration of barium in the solution drops. By determining barium concentration before and after mixing, the difference is equivalent to the sulfate precipitation. You add to it the solubility of barium sulfate in water to get how much sulfate is there. That number came on CSA-4671, came about 84 as I showed in Figure 7. I am really confident that sulfate is present in the ash. I think the problem is not whether it is sulfate or carbonate. I think there is some chemistry going on during the ashing of the fabrics which may convert the sulfate to carbonate.

Next we talk about low temperature ashing of WCA fabric (Table 9). I am starting here with very large samples, 35 gram material. As I mentioned earlier, the only variables we have is the power and the flow rate of oxygen. In the first line, we used the maximum power and 100 cc per minute oxygen. After 19 hours, most of the carbon was there, because 35 went down to 22 grams. In the second set, I said let's reduce the power and triple the flow rate of oxygen. Sure enough we ashed the material and we could see it became white. If we ash further we start slowly decreasing the ash level because each time we put the sample in, it is evacuated and some of the fiber flies away. The last line in the table gives the ash level. I am confident about this number. This is the WCA 888 again, and it is the sample that was claimed to have extremely high levels of silicon. The best part about it is when you take this white ash and you put two drops of water on it; it dissolves completely which means the ash doesn't have any silicon there. If there was any silicon, it will stay insoluble in water. The fact that you put two drops of water and it is gone means that it is probably sodium. For the CSA-4692 sample, the ash level is very high, 0.97%. It is comparable to the CSA-4671.

The data in Figure 11 are the for WCA-Fiberite, my standard sample that I am using in the CVD work. I was trying to see how consistent the technique is from one sample to another, and how good we are doing with this plasma. We are just ashing longer and longer and playing with experimental parameters. I am marking down here, the numbers that I got when all the material became white. We continued until the residue was white. Once the ash in the low temperature asher is white, we get very good numbers on it. I presume this is very accurate knowing the starting weight of the sample is over 20 gram.

- | | |
|------------|---|
| Pinoli | This is the one experiment you put a drop of water on the ash and it disappears? |
| Ismail | Yes. |
| Williamson | What temperature is that? |
| Ismail | It is near room temperature. The only heat you get there is the heat of the reaction because the carbon oxygen reaction is an exothermic. So you do get some heating and I did try to prove it experimentally or just by making calculations. The sample temperature doesn't exceed 70°C. |
| Williamson | When you are talking about the heat, is that the mass of the sample. You have not treated the fact that it is a surface phenomenon. Oxygen is attacking the surface and at that point the temperature must be higher. |

Ismail No. Oxygen attacks carbon at room temperature or even at lower than room temperature. You don't need heat to have carbon/atomic oxygen reaction. If you are talking about molecular oxygen, yes. We have to go to much higher temperatures.

Williamson It generates its own heat during the reaction.

Ismail Which means that the reaction already started.

Williamson True. But you do have heat.

Ismail Then it keeps going on. The rate of generating heat is slow because the ashing is completed in 70 hours.

Williamson You have lighted a fire.

Ismail How did you light it? The temperature is not too high and the amount of oxygen flowing in the system is low.

Pinoli This reaction is not sufficient to support combustion.

Ismail If you look at the temperature for firing of the sample in the oxygen plasma, you see it is starting at room temperature and then it goes up a little bit, reaches a maximum, and starts going down again. What I am saying is that maximum you get there is about 60 or 70 C.

Pinoli Where is that thermocouple?

Ismail Touching the sample.

In Figure 12 we talk about the chemical composition of ash (CSA-4692). the objective was to show how much carbonate we have in the low temperature ash. What I did is: ash the sample, dissolve in water and titrate against dilute HCl, using a pH meter or methyl orange. We get two steps there. Of course some accuracy there is lost because we are talking here about 1 cc of 0.02 normal HCl in your the titration. This is the best accuracy we could get with something like that unless we start ashing one pound of the material to end up with a lot of ash. To my best estimate with this procedure, which is fairly accurate. We have about 50% carbonate in the low temperature ash, while with the high temperature ash, it looks like we have 10%. Depending on whether we ash at low temperature or at high temperature, and therefore whether we ash it 500 or 600 or 700°C, we are going to end up with different amounts of ash and different percentages of carbonate or sulfate. Clearly

we have at least 50% sulfate. I would say the minimum sulfate we see is 50 and the maximum is about 91 or 92% in the ash.

Finally we jump to the conclusions in Figure 13. I am recommending not to use 950°C for ashing any carbon fiber/fabric. Be careful when you use 750°C. Maybe it is a good idea to stick between 500 and 600. Low temperature ashing seems to be a very good attractive alternative for ashing the samples. Sodium is present as carbonates and sulfates.

Thomas If you ash at 600, what is your time?

Ismail Ashing time; I wouldn't worry about it. The longest time I tried was 48 hours. At 600°C, 48 hours, you are okay. You are within the experimental error of the balance.

Pinoli That would be WCA fabric.

Ismail Yes. But for CSA, the ashing temperature was 550.

Denault You know this material that was proposed to have high silicon. Did they analyze that? How was that conclusion drawn?

Ismail I think they made a mistake, they looked by EDAX at the sample after it was partially ashed. They ended up with white stuff (which is the ash) covering the filaments, which is normal. By looking at this stuff with SEM and magnifying it, you might say, "this is a lot." It is probably a lot in volume, but it is not a lot in weight. It is a lot in terms of a blanket covering something underneath. It is not a lot. Then they used EDAX, (energy dispersive techniques) to determine how much silicon was there. With this technique, if you put any sample there, or if you don't put any sample, you get silicon. You see silicon. When you look at the peak of silicon concentration against all other species, you see a big monster peak called silicon, the rest is nothing, or a little sodium. A little sodium and a little potassium. This technique is extremely sensitive to silicon. If you even stick a piece of bread or a hamburger there, you will see silicon there. You have to be very careful when you use this technique. I wouldn't use it for the determination of silicon. That was probably the mistake they made. That is what happened. Does that answer your question?

Denault Yes. Now the other thing is if you have some new reactions of silicon, I don't know whether it is silicon or silicone.

Ismail It's SiO₂, I think. Most likely they were talking about SiO₂ or it could be in the form of sodium silicate, but how would you get sodium silicate in your fiber? That is a little bit too far to see. Unless you have a reason, it could be aluminum silicate.

Denault Then you are reacting it with atomic oxygen, so you could be making some volatile, organic silicone.

Ismail Where do you get your hydrogen?

Denault You are adding oxygen.

Ismail I am talking about hydrogen.

Denault You have water.

Ismail No the samples are dry.

Denault You could have a possible atomic oxygen reaction, unusual atomic oxygen reaction.

Ismail I would say it would be "damn" unusual. There is a possibility but it would be very, very low.

 Here are my final works in Figure 13 and my recommendations. I am just proposing some ashing temperatures here and there for the different fabrics. Of course, when we talk about WCA, I am proposing 550 to 600°C. If we are using the low fired material, I am proposing 500 to 550°C. If you really don't like those limits, I will allow you 25°C more. I think if you use 25° more, you are okay. Oxygen plasma is not a bad technique. It is more reliable than high temperature ashing, especially because we don't know where we are in terms of the high temperature ashing.

Towne In your ashing at low temperature, you said at one point you had 600 ppm and since it all disappeared with a drop of water, you assumed it was sodium.

Ismail Not necessarily, it could be potassium. From experience, the majority was sodium. The objective was to find out whether it was silica or others (sodium, potassium, etc.

Towne But at the same time, you indicated that the maximum sodium in that sample was in the 10 ppm range. You were showing somewhere in the order of 600 ppm of ash and you said you dropped a couple drops of water on it and it all dissolved.

Ismail That was the WCA, Fiberite 1986.

Towne But that WCA is still down in the 10 ppm of sodium.

Ismail Yes.

Towne Well, I don't understand your reasons for suggesting that most of that 600 ppm was sodium.

Ismail The issue I was addressing was: "is it silicon or is it something else?" In other words, think backwards. What are the soluble forms of ash and what are the insoluble forms of ash? If I asked you this question, what would be the first thing that comes to your mind as insoluble ash? Silicon. What would be the first thing that comes to your mind as soluble, sodium or potassium?

Towne It comes to mind, but it doesn't seem to make sense here.

Ismail Why?

Towne Because there is not that much sodium there. You know from test that there is not that much sodium there. My point is, if you have only something less than 12 in any of the samples you did, that just doesn't seem to fit.

Ismail It could be potassium, calcium, or some other soluble salts of other species. The ash could also be having some water of hydration. If we say it has 10-15 ppm of sodium, we could have the rest of the sodium chemically bonded to other radicals up to 100-120 ppm. Can't you? Let's say it is as sodium oxalate with some moisture in it. Let's say it is sodium carbonate with some moisture in it. That would raise your number by a factor of 3 or 4. Still it doesn't account for the entire ash. I agree with you, but the point I was trying to make there is this: if there is silicon, it shouldn't be soluble in water. If it is soluble in water, it has to be sodium, potassium, calcium, anything else but silicon. Do you agree with this statement? If there is silicon there, you should have something insoluble in water. I see your point. Maybe it is some other species that we are not after. Definitely, it is not silicon.

Towne At the last meeting I had some data, ashing results in oxygen at 600 and at 650 and it showed a significant difference in the amount of sodium as a result of the 650° ashing.

Ismail So you probably agree with my recommendation here on the temperature.

Towne Very much.

Ismail Any other questions.

Hall Thank you, Ismail, very much. A very good presentation.

Ismail Thank you.

Pinoli For those of you who are interested in the oxidation work, we are going to come back to this subject later. I might point out that Ismail has found that the quantity of sodium that you measure, using the AA technique, appeared to be dependent on the ashing temperature. The higher you ash the material, the lower the sodium content value comes out. We did a little survey on what the industry is employing with regard to ashing temperature, and found there is a considerable variance. Some people use very high temperature and some people prefer the low temperature. If one program is ashing at 800-900°C and another company is ashing at 500°C you are not talking across the table with the same numbers. The other question is fundamentally why ashing temperature is that important when you consider that all of the fabrics Ismail studied and have been fired at temperatures far in excess of these ashing temperatures. Whatever is there, must be stable because it came through the carbonization process. It was never totally clear to us what was going on and I think Ismail has shown some excellent data. Don, you should appreciate that relationship with sodium to ash content. That is something that had come up in our earlier discussions. Is there a one-to-one relationship between the measurement of ash and sodium?

Beckley I copied his line of ash percentages versus his ppm of sodium. It is a useful chart.

Pinoli Yes, it is an interesting plot.

Beckley It is a quick way of looking at what your ppm number is.

Pinoli What I would like to follow up on is, why can't we correlate this to the rayon and look at the rayon precursor with regard to ash or sodium. If we are going to control, that's my argument with sodium, it should be at the rayon level. I don't think that there is any sodium added by the carbonization process.

Denault Why didn't it go away during the carbonization process?

Pinoli The sodium? If you look up in Perry's or any of your chemical handbooks, sodium carbonate is stable to about 1500°C and the sulfate form is stable to the same temperature range.

Ismail Actually, Pat, it melts at 850°C.

Pinoli I never looked at melt point, just the boiling point.

Beckley I think the answer is that it is not carbonizing oxygen and therefore the stability is different than when you stick it back in oxygen.

Pinoli I missed something in your statement, Don.

Ismail It is present inside closed pockets in the fiber and you cannot get it out.

Pinoli Okay, let's move on.

The next subject that we are going to be picking up on is SPIP product identification code. This is in response to a specific request of NASA. Corky Clinton asked us to look into the rationale and the possibility of introducing product code identification that would allow any engineer in the field to fully understand what product he is working with. Case in point, everybody recognizes that we deal with MX 4926. I am just using it as an example. If you buy MX 4926 prepreg, it turns out you don't know what type of fabric is in that prepreg. There are so many versions of MX 4926 out there that I know that NASA was getting frustrated trying to cross-reference data. The need truly exists to improve product code. Either put a separate code onto every variation that the prepregger makes and/or carbonizer produces. The impression I had from our last meeting was the vendors are reluctant to do that. You can appreciate everytime they make a product change a new product identification is needed. This would go on forever like a roll of toilet paper. What we did at the last meeting was to decide to table this and put a subcommittee together of Jack and myself to look into what could we do with regards to coding of the products, so that the average engineer could understand the product. Beginning with this first viewfoil, I will go into my contribution on this and then Jack is going to cover the prepreg issue.

What we did is separate carbon fabric and prepreg. I find the fabric a lot easier to work with and Jack understands prepreg.

For a carbon fabric cope I think we need precursor type, whether it is PAN, rayon, etc.. We also need the source, whether it's AVTEX, North American, Groupo Cydsa. We would like to have some indication as to the denier, filament count. We want to know if its prewoven or post woven, fabric construction. Is it eight harness, five harness, etc. We want something that gives us a feel for the firing temperature of the fabric. Is it low fired, high fired, intermediate? Under those considerations, I looked at two aspects, one is moisture adsorption capacity and electrical resistivity. I felt that these two numbers pretty much give you a handle on firing temperature and fabric properties that are important. What I did was break down each issue to

critical points. Precursor type would be R for rayon, P for PAN, for pitch fiber I used M for mezophase. Precursor source would be Avtex, North American, Groupo Cydsa. What I like about using standard connotations, even the novice would understand that R stands for rayon, P stands for PAN. Just by going through a code and you see those letters, you almost automatically know what they are. Going on to precursor yard denier, filament count. Obviously, 11 would be 1100 denier, 16 would be 1650 denier and K would be the filament count. 1K, 2K. I was looking at filament count in terms of the PAN fibers. If you are looking at rayon, then you have to say, for example, 720. Prewoven, postwoven. Postwoven is just coming into its own, but we think it is going to stick and be around for quite some time. Also if this code is going to be applicable to PAN fiber, all PAN fibers are postwoven. You have to have it in the code somewhere. On weave, PL means plain, NO means unknown, or not specified.

Mills Are you going to specify the number of plies? For example, 1-ply, 2-ply?

Williamson Twist also.

Pinoli Who's taking notes here? I need someone to take notes on these questions.

Ismail It is already recorded.

Pinoli It's on the record.

DiMeo I guess I missed it. What is this for? Who is the novice out there?

Pinoli Here is where I think it would be effective. We as a new program want to order material. We want to call up your buyer and place an order for a product called R/A/16/A/8HS/16/46-55.

DiMeo You called my buyer and said that to him.

Pinoli Yes. Say Thiokol wants to buy some of this for the ASRM program, using an SPIP code. The SPIP code in this case would identify Rayon, Avtex, 1650 denier, prewoven, 8 harness satin, 16 would reference moisture adsorption capacity and 46-55 would be the range for electrical resistivity. This code identifies exactly what I wish to purchase. If somebody from NASA wants to know the product, you simply give them the SPIP code identification number. This is really an abbreviation and if you would like to put some properties out on that particular material, you could reference the SPIP code. If that code is simply put into your documentation somewhere, anybody with a little intelligence can unscramble it.

DiMeo I think that you are making the assumption here that everything is called 4926. If that was the case then this would be pretty good clarification.

Williamson Give me a chance, will you?

DiMeo If you had a PAN fiber, it would be 4926. For instance, if you were going to buy 4946, you know what you want to buy. You personally know. Now if you are throwing this out to a guy who doesn't know anything about composite materials or ablative products, in particular, and he looks at this, he has to go look up this information to figure what that is before he can figure out what the product is.

Pinoli That is right. He has to have a method of unscrambling the code.

DiMeo That's right.

Pinoli Jack has used a different twist on that.

DiMeo I guess I am just fearful that we are throwing more confusion onto some existing chaos.

Mills The problem, I think is that if I buy MX4926, if my buyer goes and tries to buy that, he can get VCK-based material, he can get CSA-based material and in other extreme conditions he might even be able to get VCL or CCA-3. All of which he would sell as 4926. If we are going to try to make some generic specifications of industry standards, something like this may be appropriate.

Hemmelman It really is a specification if you stop and think about it. The firing temperature, moisture adsorption and things like that. It really think what this does, every prepreg spec references a fabric spec. I think we ought to point out a fundamental defect in our system that our fabric specifications don't have all the information that is really required. I think that is really the problem.

Mills Right now you have to go through a chain of specifications and in certain cases, my buyer, because he is going to a computerized system, he is looking for something like this that he can put into the computer that is no more than 16 characters long that will uniquely specify the product. By uniquely, I mean it is an 8 harness satin, low-fired carbon.

Williamson You guys have absolutely destroyed what I was going to talk about.

Mills But as far as my buyer's concerned he has not discriminated between two products.

DiMeo You don't have your buyer just come out and buy material without specification.

Mills No, he's got a computerized list and this is the way we are told the world is going, he will have a 16-digit code for an IUS application or a Titan application, or whatever, that is the same code if the materials are identical. Even though one of them is certified to SEO865 and one is specified to 4MDS40721. If the requirements are identical, he's is going to buy material 1, 2, 3, 4, 5, and that is the way he is going to order it from now on. Now what Pat is talking about, I think is more in terms of advance materials. What I am talking about is production materials. Making a case for the advanced materials having quite the same amount of standardization is different because you will be dealing with developmental products that may never go to production and that I think would complicate the issue. Also, I think there are some people who are concerned about proprietary things.

Williamson I am glad these kinds of things are coming up because that is what I want to talk about.

DiMeo Let me just clarify one thing. If you order 4926 without specifications, you would not get 4926 with VCK. That is because the price of VCK is substantially higher than VCL, CSA, or CCA-3.

Mills That is true today. But say the supply of VCL, CCA-3, CSA dries up and all you have got is VCK and I am willing to spend whatever it costs.

DiMeo It is the same rayon.

Mills Maybe there is a stockpile of VCK that there isn't of VCL or CCA-3.

DiMeo VCK is made with 1100 denier yarn, where VCL, CSA, and CCA-3 all start with the same rayon fabric.

Mills Right now NASA is using the 1650. They have got large demands in terms of quantities. Suppose they corner the market. Avtex goes out of business and all the rayon is in NASA's possession, and I want some for a commercial product, I am willing to pay for it. There are cases where, if we could get VCK you would sell it to me and then charge me the price.

DiMeo I will sell you anything you want.

Thomas Ed, don't you think your buyer would say I want, he wouldn't just say 4926. He would say I want North American yarn, or Avtex yarn.

Mills No, he does not. As a matter of fact I have just gone through some problems in this area where we are computerizing and we have bean counters doing the ordering that don't know the difference between pitch and PAN and rayon and anything else.

Thomas That code isn't going to help them any because they will have to have all the data to read it.

Mills No, but I can tell him that he wants Pat's code, whatever it was. If I have a code by which I can tell him what to order and the code is 16 digits or less, he can put that in his computer. I haven't specified yet whether I get U.S. Poly or Fiberite, but I have specified or I have a vehicle for specifying that I get 8 harness satin, low fired or I get 5 harness satin, intermediate fired. That to me is more important than an engineer using it and my quality people are simply checking off that it conforms to the spec.

Williamson I am going to make a remark here. I am wondering why I am here. This has bothered me for a long time. I realized that there is a Mafia, a big Mafia and there is a small Mafia. The Big Mafia has a godfather, and the little Mafia up at Lockheed doesn't have a godfather, it has Pat Pinoli.

What I have done is that I have taken two candidate materials on the ASRM program and identified some of the attributes and God knows there are a lot more than I am treating here. At the end of this we are giving you the opportunity, Everyone is going to get a copy of this and we are going to ask you to comment on what attributes you really want to have included in the identification description and after that we are going to key in the applicable specifications where it is practical so that when we get a, as we get into a final mode on this thing as to how we want to identify the collection of attributes that are associated with the material. We are going to put that up in, at the minute we are going to put that up in ——. You will have it on a disc and your bean counter can put it in as system and you will have the product identified.

4996 is a unique material. It is specifically tailored in response to specific requests. These in general are the product forms, I have put this in here because sooner or later this will happen. There are many more attributes and we are going to give everybody in the committee a chance to comment on these. I want to make a comment. I brought out items that are sole source, not for action, I just identified them. I have a great deal of admiration for North American Rayon. The reason that I am beating the drums, maybe, for an alternate source is the fact that both NASA and the Air Force are concerned with a sole source rayon. We have gone through this thing for 28 years where we have a source that disappears. I believe in rayon, I started with rayon. I have been in this thing since 1940, never mind. Anyway, the

reason for having an alternate source of rayon was to stop the stampede to PAN. It is as much for North American's benefit that we have an alternate source of rayon as it is for the industry. What is good for the industry is good for North American Rayon. Now I have touched on that, and we are happy that we are going to have somebody tells us and show us about rayon. It is out of this type of information that we would like to attributes that you think are the most significant and belong in an identification code.

This is probably obsolete because Polycarbon is delving, what I am saying is that Fiberite did develop a surface finish for prefired yarn which would go into postwoven fabric. They have agreed to supply that to the industry with some stipulations as to protecting their proprietary position which I think is highly proper.

The resin SC1008 has been around thirty odd years. It is supplied as an alcohol varnish available in drum lost, tank truck or tank car if you want to order the tank car. It does require storage under refrigeration. It is a non-proprietary and in general use by the ablative community. This is what I think what Pat would love to see on every single item on the agenda. That isn't always possible. I am going to bring up a point. High purity carbon, I guess it is actually submicron in size and I question this categorization. It comes from a Canadian petroleum industry source and they have been very careful to point out that it is not the same filler as 4926. I think that is getting pretty specific.

This brings up another issue. It is a foreign source.

Ismail

Who makes this filler?

Williamson

Let me put it this way. I have tried to respect the information that has been given me by both Fiberite and U.S. Polymeric. Those questions are better addressed to them. Now what I want to bring out is that if we say we want to limit our materials to those produced in the continental United States, then we will have to shut RSRM down. We will have to shut the space shuttle program down and you will have to shut off the Titan IV program, because essential materials to those programs are not limited to continental United States. So are you going to make the rule apply only to our ablative materials on the ASRM program. What I am saying is that the foreign source can be categorized two ways. One, it is on the North American continent, which from DOD's point of view is far different from one that is not on the North American continent. Our nickel comes from Canada, so pointing a finger at Group Cydsa because it is not in the continental United States, I think is beside the point. There may be those who disagree with me. I cannot accept as being very serious a point of fact that it is not made in the continental United States. If it is

made on the North American continent because it is available. We will never need a Desert Shield.

I am going to talk about 5939 which is a Polymeric material. It had an old designation as 5055 Improved. This is a very old designation, just like 4926 is. It categorizes the family of materials. We have gotten to the point where designers and end users are very demanding and can be satisfied only with specific materials on which the data has been generated in sufficient quantity and has been qualified sufficiently well, so that it is reliable. In order to insure the continuing reliability of the data that is used in the design and to determine the functionality of the hardware that is made. You have to be sure about the raw materials and that they are controlled.

So we start looking at, first of all, the manufacturing process. I am going backwards in order and this is just as important, if not more so than the raw materials, and the product forms that are available are the same ones that I discussed in 4996. I am going to talk about the raw materials. Prewoven carbon fabric, the carbonizer is BP Chemicals, Advanced Materials Division, process is pre-ox two-stage, long time, low temperature. This is just to bring out the fact that is not a short time cycle. The final conversion, short time high temperature cycle, I understand, has been defined very recently by Thiokol. Is that right?

Beckley

Effectively, the program definition is going to take a little, we are going to determine that as we progress.

Williamson

This, I think, belongs to the processor. He makes his own arrangements with the procuring agency and it will be covered by specifications. It is our hope that when we get through and we make a decision on what attributes we want to enumerate that we also list the applicable specifications with it so that as an identification document, procurement people will have it and don't have to get into the details of specifications because its specifications are cited and I think we do possibly have a way to handle in our more advanced information systems a codification that will do the job we hope to get accomplished. I am using some help from Appleton. Sorry I wish I could have talked to you first, but I used what was available. We intend to put this up on a disc and I will furnish 3 discs when we get all through, Pat, and we can go from there.

I am sorry for this. I am living in the past by putting that in there. I understand that those are high speed rapier looms. It will have a treatment on the selvage, because in a rapier that becomes a matter of concern.

Drake On the rayon yarn you are listing the supplier as North American on the 5939. Would it be the same product if it were from another rayon manufacturer?

Williamson I am not prepared to answer that question. That is something that our committee should answer. That is why I am putting out a lengthy write up on this. There will be a sheet with a list of attributes on there and this becomes a question of supplier as a necessary attribute, the supplier be identified. That will be coded in there.

Beckley Ken, as a background, our grade code system which is what that 4-digit number effectively is would handle that with a suffix letter. A, B, C, or D to denote a change from the original to an altered product. The definition of North American for this product is once again by programs intention to use North American only at this point in time.

DiMeo If a second source for rayon was developed that was identical to North American's current rayon, you wouldn't change the identification.

Beckley We would, just by the way our system works, have a different suffix letter.

Williamson I would like to bring out a alternate point if I could, Don, in that the rayon acceptability will be covered by specification. If it meets that rayon specification, does that preclude the use of alternate rayon that meets the specification that has been approved, it's not a QPL, and the scheduling and purchasing and manufacturing may be aided by being able to move from one rayon to another. Do you want to exclude that?

Beckley Jack, everything you said is really correct, except that we find customers like Ed Mills, who want to have a reference to the fact it is the different source and this is the easiest mechanism that that type of thing ...

Williamson I am not precluding that. I am going to leave that up to the committee, SPIP committee.

Beckley It happens that if you take shuttle RSRM and it has a very pervasive influence, they have gone through from CCA1 to CCA-3 to what, effectively, will be CCA8 from North American Rayon and that is 3 different precursors, and they, in their own system, can't cope with a suffix change from the one they started with back in 1975. There is a customer that says I don't want the change. Effectively, what we see in the real world is we have people who operate different ways and this is the mechanism we have to account for both of them.

Mills Let me say that we are, I don't know about shuttle, happy with that in terms of the denoting 5055 as the basic product with no suffix means it is basically the old Avtex, with a suffix N or a suffix A, or whatever to show that it is NARC, or B is Grouped Cydsa, or whatever it is. If I don't need to specify the detail, I specify FM-5055 and I don't care whether it is any of the three sources. If I need to specify it, I specify FM-5055N. That seems to me to a very effective way of handling it.

DiMeo If you don't specify it, is it Avtex?

Mills The way it is right now, that would probably be true, but if we are going to develop a new system, where we assign a letter to an Avtex material, and a different letter to a NARC material, and a different letter to whatever we come up with next year or three years from now, then we would have an effective system.

DiMeo We are developing second sources, not different sources, perceived to be identical sources. We have got to have one source for rayon which was Avtex, then we developed North American, grade 23 to be an identical source to Avtex. If that is relatively true, you go down to the electroscopic level and prove that. You have three sources for carbonized fabric. You have two weavers. You do this for a couple of reasons. One is to protect the supply and one to protect the schedule. If you say I want FM-5055 or 4926 and 16M and all this, that product might not be in the pipeline to support your schedule. Do you see what I am saying? Suppose you need delivery of that product within 6 weeks, and you say can you get me some 4926? Yes, I have some in the pipeline, but if you want specific variations, it may take you 24 weeks to get that.

Mills That is a very big problem.

DiMeo You are requiring for a generic 4926.

Mills No. My requirements are never for a generic material. My requirement is for what is qualified for that program. Now, your argument that we have developed an identical substitution of NARC which is identical to the Avtex and something is going to be identical to that, there are no two products that are identical. They may be functionally equivalent, but my customer may require me to do a qualification effort for what we are talking about as the alternate to the NARC. I may have to spend 6 months and \$6 million to prove that this new material is equivalent. I cannot afford to and my customer, whether it be the Navy or the Air Force or NASA, are generally consistent on not allowing me to make a substitution without their permission. There are standard "no changes" clauses and one of the things is "geographic location of the facility". I have to go through a qualification effort or at least through an effort where I present to my customer the argument and the data

that says the material is equivalent. I cannot afford to have a vendor making changes without notification and approval.

DiMeo Ed, I was not implying that we would take the liberty of substituting any product in.

Mills I don't think you would. I am not saying you would.

Williamson Ed, you make a wonderful straight man.

Drake One of the important things of product identity is determined by program by program qualification staff. If they are not on the QPL, you can't use it.

Williamson This is part of what we proposed to do. There will be applicable specifications including the QPL. To what degree we can pull this off, I don't know, but we are going to grapple with the problem and I will be up here again I hope. We will have some handouts here later today and in it there will be a sheet with an attribute list that we would request express their preferences. We can't list them all. I went through there and I identified about 50. What we would like is a consensus system. Which of these attributes are really determinants as properly characterizing the material. I thank Ed. No one person is going to say, we need a consensus, and we need to gather as many opinions as we can. We are going to try and categorize those and then go back to you and say, here is the way we see it. This can be handled with this information system that we have proposed and we would like an expression from you as to whether we should go ahead with our second cut.

I want to talk about this for a minute. It is true it is a proprietary, sole source material, but it is available. John Chang has offered to sell it a number of times and I am going to go back in history. I don't know whether you remember a guy named Schmidt, I think, and before 91LD and before the Air Force approved the use of 91LD. They said look Elmer Worken, you are a little guy. Ironsides makes emulsion materials for Owens Corning. They do make some resins. We are a little antsy about writing this in without some assurance that if something happens that we can still get the material. So it was required by the Air Force that the manufacturing specifications, the exact SOP, be produced and it was given to the Air Force. It would be available in case of eventuality of need for another source.

You know that the fact that whether a filler in a product is submicron, and the petroleum source is foreign a foreign source, this kind of information is privileged information. This information really belong to Polymeric and Fiberite. I take issue with some NASA philosophy, you know. The Russians can buy all the specifications for the space shuttle for like \$25. They bought 100 copies when it was first made available. I am not sure that this kind of information should be in the public domain.

I am against it. You know, take a look at the world. In war you have allies, you have friends. In business, you don't have any allies, any friends. I think that is proprietary information. I think it belongs to U.S. Polymeric. Fiberite has the same thing, it belongs to them. We want to use it, the community wants to use it. We shouldn't abuse it. Now I have said my peace.

Ismail Can I just add one little thing. I don't think the filler is that big of a deal because a filler is a carbon black. There are millions of carbon blacks. I don't think that this particular number of carbon black was selected on any scientific basis. I don't think, I mean if we were talking about fibers, I would say yes, you would have to be careful. For filler, carbon black, I don't see any secret. If you give me a sample, I will check it for you and I can get you exactly the same one. I am sorry to say that, but that is how I see it.

Williamson Most carbon blacks which transfer into graphite readily and some will resist it.

Ismail Sure.

Williamson Carbon blacks that are used here are those which resist transformation to graphite in order to reduce the thermal conductivity. The other thing is that they go through temperature extremes and do not change form. Not all carbon blacks will do that.

Ismail I didn't say that all carbon blacks are the same. I am saying that there are millions of them available commercially.

Williamson That is the other half of the problem.

Ismail I don't see what secret you want to keep away about carbon black.

Beckley One comment that I have heard is that the fellows who studied rayon for about three years finally concluded that that innocent little rayon spec was really defining a unique material. I don't believe there is really much difference in the innocent little spec that defines this particular carbon black. They are both inherently unique materials. The more you get an opportunity to study this, the more you will have an understanding of how they fit together. Just as a friendly to you.

Ismail Each carbon in this world is unique. I will agree with that. I don't think that this filler is a lot more unique than thousands of available commercial carbon blacks.

Beckley I would like to do one more thing because I think there is another dimension to the subject presented this morning. The two products that Jack chose to characterize are

effectively candidates for the ASRM program. They represent the product of the best thinking of the two prepreggers, essentially working on their own and spending their own funds trying to develop the best product for ASRM as ASRM has asked for it to be. We are both undergoing a very unique relationship in that for the first time the development is being done in conjunction with a separate materials team from ASRM. There is a very close working relationship on this, deeper than any we have every entered into, in trying to bring on the best product. The thing I see happening here this morning is I think unfortunate. I think it is kind of a timing issue. With ASRM, they have guaranteed us a degree of proprietary anonymity that says they will keep the information proprietary within the team until such time as the product is essentially chosen. What I feel disturbed about is that with that relationship with ASRM we have SPIP apparently saying that they would like to spread the whole character connotation of these advanced development materials. Essentially only one material will get chosen and then that technology that has been applied may be usable somewhere else, but if it is spread and given away at this point, its value is gone to those of us who are spending our money for it. I would really like to request your indulgence to understand the timing issue and let ASRM do their thing before we get around to spreading a 10 character fabric and a 14 character designation for prepreg which in effect, carried to the degree Jack digs into it, will be a complete revelation of a set of technologies. It is just not the right time for it.

Williamson Don, it will not happen next week. This is a long term problem. We will not violate the proprietary positions.

Beckley It is just not ready yet to be done.

Mills I agree on an advanced material, it is probably not appropriate, but for different reasons. When you are dealing with an advanced material you need the flexibility to make changes in the product and maybe 5901 doesn't work, so you go to 5902 and 5903 and you have a hundred variations. You are going to end up with a hundred variations of what you put into your matrix into the product codes. I would think that as a better way to do it would be to let the advance people work in the dark in their own entity, proprietary if you will, and once the product goes into production, that is when I think that this coding becomes a lock on the product such that if we change something like the rayon source after production. That is where I would be more interested in seeing the coding.

Beckley Then effectively, that is what has transpired over twenty years with the product that we have talked about this morning, the 4926 and the 5055, becoming a known entity. The step in between is to have a baseline document which is everyone of the details right down to the operative documents that are the bible for that product. They are

on file and accessible to people who have a need to know. They are not accessible to everyone at large. There are degrees of timing that are appropriate for products development stages and productions stages and finally to the point that it is Ivory soap and everyone knows what it is.

Armour I think, Don, for the benefit of this group here, that selection or that material will be available as will described for everybody in about 12-14 months from now. We are studying about 10-12 different materials, and will be and there will be a down selection in about 8 months to two materials and then from there it goes to 1 material in about 12-14 months. There is a lot of proprietariness in what we are doing, in what the prepreggers are doing and the materials they are trying to develop.

Williamson I am going to ask a question. I have heard that all materials that are ASRM when you get all through is going to dual-sourced? It is not going to be one material.

Armour That is correct.

Bhe Jack, I still do not quite understand what the purpose of this product identification code is. I have been sitting here and trying to. 5055, people know what it is and 4926.

Williamson We were asked by a members of the community and by NASA and by SPIP to do this.

Bhe I still not clear why we have to come up with this letter code in 16 characters or less. The other question, have you guys looked at the resin? Right now, Fiberite's SC1008 and U.S. Poly's 91LD.

Pinoli He is not going to specify any products. The only thing he is trying to do is identify what that product represents, what you are buying.

Bhe Right now, pretty much, the ablative community knows what MX4926 is.

Drake MS4926, for example, could it be intermediate fired or is it just low fired or what.

Bhe We have specifications.

Mills What you have is your specifications that controls it to your satisfaction as your company requires it. My specification for one program controls it for that and for another program, I have got another specification. For ten different programs, I have ten different specifications. All of which might be 4926, for example. Some of which I might require low fired only, and some of which I may require high fired

only. I think the purpose of this is to get an industry wide designation system, since we are all going to computerized ordering systems, at least I am told we are. We have just done it and it is a major heartburn to me, in trying to get a workable system. We need something like a 16-digit product code that we can put in that will uniquely specify material, whether it is used for IUS or Titan, is immaterial. My ordering people need to be able to order a product that is generic to a degree and yet unique to a degree. That is I believe the function of the product code, the function that is most useful to me.

Buechler Wasn't it also intended for this code to provide a means of checking material property data once it has gone through the various testing procedures, so that you can go back and compare apples to apples in terms of what was tested so that you don't have to go back and repeat some of the testing? You know that the material was tested by this code and you can identify that it is very similar to what you are intending to use.

DiMeo That means that there has to be a spec code then, too. The material can't be tested by that code.

Williamson No. That is what I was saying. You have to go back and identify and bring in the applicable specifications. Those in turn follow our test methods.

DiMeo When you order a 16-digit code and let's say that two weavers are qualified for your program, both Avtex and North American are qualified, plus all three carbonizers, you are ordering a product that is essentially generic and there are 25 combinations. Does the purchaser want to see twenty-five 16-digit codes when he could really say 4926.

Mills There are literally cases where I have a parts list which I am required to have by the various DOD specs that apply to me. I have a parts list that has 16 alternates for a single material. That is unfortunate, It is the way the people that write the DOD Std-100 and the various things that tree off of that have deemed appropriate to handle this. I may not agree with it, but I have to live with it.

Larson I think that first of all, it cleared up one question. Do you request that Corky Clinton relate the whole of material identification? Is that correct, Pat?

Pinoli Material identification?

Larson Not relating to test data.

Pinoli No. The point is he needs materials identification on the test data. In other words if he gets property data out of SoRI and it simply references MX 4926. That isn't enough. That doesn't define the product and we don't know whether we can use that data for comparative purposes. MX 4926 can be produced through a whole range of filler concentrations which are controlled by the manufacturer or the end user.

Armour Pat, if I were going to send 4926 to Southern Research to get tested and spend a lot of money, I would certainly know what it was.

Mills Normally you will give them the pedigree including who processed it, what the hydroclave pressures were, everything.

Pinoli You know your data, but if I am an outsider I don't know where it is.

Mills Normally, in the beginning of the test, SRI (Koenig) will publish everything I give him in terms of pedigree unless I tell him something is proprietary. But you now have to go through and read the text to figure that out. Having a product code that you can stick in front of the data base is a real key point. The code needs to include number of filaments for rayon, i.e. 1650 denier/720 filament and 1100 denier /490 filament. Also the number of plies and twist and direction. WCA is 3 ply of 1100 denier. VCK is 2 ply of 1100 denier. VCL/CCA-3/CSA is 1 ply of 1650 denier. The source of carbonization and prepreg should also be included to facilitate tracing problems as well as to support some uses which have only qualified one manufacturer even though others can meet general requirements of spec. We need to know the resin source and filler, whether it is 91LD, SC1008, etc. Concerns should include ability to specify product for production primarily. Advanced products under development should have flexibility to change and at the same time allow proprietary details until material goes into production use. Code should be limited to 16 or less digits consistent with Cullinet and other procurement systems which are computerized (standardized).

Pinoli I don't recall much data coming out of source that tells me what the product specifications were for that MX4926. If I were to read SoRI reports, I don't think I will find reference to your specification for MX4926 in there.

Mills If you have looked at any of the ones in the last two or three years you will find them.

Pinoli If you dig at it long enough and tediously enough, you can get back to zero. It will cost you a fortune to do so.

DiMeo Why would we want to segregate ourselves?

Pinoli We are not segregated.

DiMeo Every program has its own specifications that it feels is unique to itself. Every agency has its own set of requirements. Do you know that when we make 4926 or 5055, we make it the same way for every program? Do you know that? We use the same fabric. Coming off the same lines you get shuttle grade, you get D5 grade, you get peacekeeper grade. The only difference is shuttle grade is certified. When we mix resin for D5 grade, shuttle grade, peacekeeper grade, it is all the same mix card. The resin is mixed the same way and impregnated on the same treater. The only difference is that at the end of the line the QC lab says shuttle, D5, peacekeeper. That is the difference.

Mills But it is Titan that is 5 harness satin.

DiMeo Ah, VCK fabric. We can change that designation, if it really bothers you that much, Ed. We can call it something different.

Mills The problem is that we have got ten years worth of nonchange

DiMeo You are going to spend a lot of money to say that NARC is the same as Avtex.

Drake We have had problems within Aerospace with the designers and the thermal people not knowing which fabric it is. I have surely been confused by the data base that we are using and what it meant.

DiMeo VCK versus VCL, CSA, CCA-3. That is what you are referencing. Because if you take the three low fired, lower fired materials, is there that much difference between them? You can prove there is a difference, but in that motor, does that nozzle know there is a difference?

Drake In the case of the IUS and a several hundred million dollar payload, and you have fired one and not the other, you really do care.

DiMeo I am not saying that there is a mistake here, but in the generic fabrics, can you tell the difference?

Mills When we go through a qualification effort, you start off in development and the you qualify your design, having picked what materials work. If you are dual sourced, you have to qualify both sources and all the various combinations. You have to fire one of them. In IUS, we fired maybe a dozen motors with U.S. Polymeric material and similar number with Fiberite. There are things that happened downstream that have changed that, but at the time that we were qualifying the MX4926 which

happened to be a VCK material versus the FM5055, which happened to CCA-3. That is the way it is done. You can make an argument that I have qualified a CCA-3 so I can slip this CCA-3 into the Fiberite and vice versa, but that is not the way the trees work and that is not the way our customer seems to want to make it work. If the customer wants to change the rules and say that I can use a generic product and I don't have to qualify all the variations, I am willing to live with that. Right now, Navy doesn't say that, Army doesn't say that, Air Force doesn't say that and NASA doesn't say that. I don't have many other customers.

DiMeo We are spending an awful lot of money with the North American qualification saying we have got to know every variation of prepreg, every variation of fabric, weaver, and whatever and every component in the nozzle right down. For thirty years we can't determine as an industry that this is the same. VCK is the exception. It is a different...

Mills Let's back up about 1978, 1979 vintage. We changed from IRC to Avtex and that worked. Later we tried to substitute American Enka. That didn't work, even though it was "the same". Now we are going to NARC and yes I feel that a lot has been done and in all probability, it is perfectly equivalent. Can I prove that? No. Not without a qualification. I can wave my hands a lot. I can put a lot of numbers on paper, without some test data as in physical properties and as in ablation performance, as in conductivity which may in fact be slightly higher for the NARC material in some circumstances. I get back down to my customer wants to see a firing. He has a billion dollars riding on this thing and he doesn't want to talk about a million dollar effort to qualify a material. Just do it.

DiMeo Granted. You have to look at the data to see if it works. Let's take the example that you gave. Take North American and you give it to Amoco and you tell them to carbonize it and they carbonize it and it works. So you make prepreg out of it and it impregnates and tape wraps and it cures and you make some nozzle and you machine it. You fire it and it works. Then you get the same rayon that is a Polymeric and they carbonize it. If you look at the fabric datas and compare the two, compare them down through the histories, you know that BP's prepreg works. Why should you have to fire it? You have proved in the past that this prepreg works the same as my prepreg works. I can say that because you interchange the prepreps almost universally, yet we have to go and prove it again. Suppose you change the rayon. You have to go and fire every variation.

Drake The user, the kind of vehicle we are going to put into orbit, really demands it.

Mills The user wants to see the data supporting the qualification.

DiMeo After thirty years, you guys are telling me we have to do it again. This is not directed at any one of us. I am saying this, looking into a mirror, to myself. Sometimes I wonder what we do.

Mills You are making the same argument that my program office makes routinely, that my purchasing office makes routinely, and that I have even made on occasion. I always lose when I try to fight for your position and I always win when I go the other way, because I have got the customer who wants me to do it that way, and the customer is always right.

DiMeo With every variation of every material that you could possibly get in every location. You have how many sets of data base? You have a statically significant data base that you are throwing out the window because you have to have three more.

Hemmelman Has anybody thought of the ramifications if one of these qualifications of North American Rayon doesn't work? What the industry is going to do? Has anybody thought about that?

Drake I think the answer to that is that yes, we have all thought about it.

Pinoli I love the stimulation of thought on this subject, but we do have to move on to other facets of this effort. I think we are going to continue to explore this issue on a subcommittee basis and I am sure we will be contacting individuals along the way for the next meeting. Now we have a few things we want to accomplish before lunch, which Bill tells me will commence at 12 noon at the pool.

There are two subjects that are on the agenda that I just want to briefly discuss and move them off the agenda because they are relatively new to this committee and the intent was to get some visibility to these subjects.

An SPIP initiative to adopt a water-soluble rayon yarn lubricant and size for weaving. At the present time North American Rayon is putting a lubricant onto the yarn and the purpose of the lubricant is two-fold. One is to allow NAR to spool the yarn and have it stick sufficiently that it doesn't slough off the spool. Is that right. Bob?

Looney A lubricant to protect on friction abrasion.

Pinoli Okay, that is another aspect. I understand you need a sizing on your yarn to allow a tight spool to be wound and hold the yarn in place on the spool itself.

Johnson I am taking up two issues as far as the lubricant on the yarn, number one the producer needs it. As I told you Avtex, we worked with Avtex trying to get some

yarn that 0 finish and it looked like a dog's breakfast. It was terrible. They needed a new process in order to make a decent yarn to keep the filament from going all over the place. Secondary, they needed it due to the friction so that the lube wasn't all on a piece of fabric. Both producers need it all the way through until the time they make fabric out of it.

Pinoli

Okay. The bottom line to this is the carbonizers inherit the fabric with sizing on it and the first operation they have to conduct is to get it off. There are no attributes for having a sizing or lubricant on the product prior to carbonization. We have seen some work conducted by Amoco that shows the sizing had a definite detrimental effect on the carbonization process. We have made modifications to the sizing system being employed at North American. We don't think we have that big a problem, but environmentally we have a problem coming with regards to solvents employed to remove sizing from yarn, especially chlorinated solvents, in California. If they go up the stack as being affluent, you will be fined. More and more, we must try to eliminate chlorinated hydrocarbons. Well, the easiest way to do that would be to have a water soluble sizing that could be easily removed. Another alternative would be to use a sizing that is not detrimental to the carbonization process. In other words, just run it as is and not worry about it. Whether that is a practical consideration, I am not sure since I am not in a position to speak for the carbonizers. I think the end users must confront this issue pretty quickly. Otherwise the carbonizers may be forced to stop production. What has been asked of me is to put this issue on the agenda. We have one major program coming down the road Bill. That is the ASRM program. Is it possible that we could investigate this particular issue within the confines of ASRM to see if we can qualify a material with an alternate lubricant or sizing on that product. What will be required to pursue this issue is a sponsor. There is no way either one of these manufacturers, North American or the weaver, can institute a change of this nature without a sponsor. Somebody has to stand up and say I recognize this potential problem and we have to do something. Let's do it in a constructive manner. That means working something out with North American, the weavers, and following it through the system. Do you think we should combine this together with specification limits and a few other issues? Would it be appropriate to set up a little task force aside on this? Yourself, myself, Kim or Cindy on it, to look into this issue and report back in six months. Do I have agreement from the carbonizers, Tom, Don, for a cooperative effort?

Beckley

We know it is a problem. We believe that sooner or later we will have to come to the community with an answer. I would be presumptuous to say that we know what that answer is today in terms of the alternate finish. You have defined the problem. It has to have something there at the present time, and it has to be removed or a carbonized material is not carbonizable, so we will have to find a substitute and to

some extent I am not prepared at this time to say that we need any additional assistance other than at the time there is an answer available we need the tool effectively carried through an effective changed policy. The no change clause would in effect, say, you have got to throw it up in the air and then it becomes an item that is going to get a certain kind of qualification activity done to it.

Pinoli I want to be sure that we all understand that you don't classify this as a proprietary study.

Beckley It is very definitely a proprietary aspect. It started back in with the proprietary nature of the finishing with Avtex and has only been revealed to a limited degree outside of North American, so it is not general knowledge to the nature of that product.

Pinoli Are you referring to the sizing that is currently employed?

Beckley Yes. There will probably be more than one potential answer later on.

Pinoli The proprietary nature of the Avtex sizing was Avtex's proprietary consideration. When it was dumped on North American, it was no longer proprietary at this point as far as I am concerned. Bob, you don't treat that as a proprietary issue, do you?

Looney No we don't. We think that the finish is something that is largely between the weaver and us as a supplier and then the carbonizer will get it off whatever it is. As long as it functions successfully for our use and for the weaver's use, then removal is going to happen regardless. We have no qualms about revealing what is used on it. In fact, we stand ready to be able to supply quantities from laboratory size to full production size for evaluation purposes. if a sponsor is found to promote. We are not going to initiate anything ourselves, but we stand ready to respond to it.

Pinoli I think in the past one of the things that has created problems was the fact that Avtex treated it as proprietary. We had a lot of problems understanding the significance of that sizing that was applied and the difficulties in removing it. I would like to bring this out into the open as far as the industry is concerned. I would like to see a common sizing or lubricant applied that all the manufacturers, this would go across the board, whether it be Amoco, Polycarbon, or Hitco.

Bhe Sizing is not going to affect the end product any way.

Pinoli That is correct. It shouldn't.

Denault I thought Amoco demonstrated that it did.

Bhe No, that is going to be removed.

Pinoli It was removed.

Denault What was the effect of the sizing when you didn't remove it?

Beckley The material is basically non-carbonizable. It becomes a monolithic structure instead of a set of filaments that are inherently released from each other. It is bonded into a unit and it becomes very brittle. The background on this is that it started out with Avtex and every finish is one of the things that a weaver or a finish supplier vary seldomly guards so Bob's benevolency in opening up this one formulation does shed a differently light on it, but I am just not certain where we will end up if somebody wants, has a new one to develop and wants to release it, that is fine. Today the formulation that I have heard of and know a little bit about has about 8 or 9 ingredients in it. So I think it is still a pretty complex animal and it is, thus far, unique and we are all working with it and it does come off.

Looney I am not aware of what the producer has to put in it.

Beckley You but a sizing?

Johnson Pat, isn't it true that basically, you don't care how you get it off as long as you can get these issues? You don't care what you put on it as long as it works.

Pinoli Sure.

Johnson From conversations that I have had on the subject, if you can wash it off with something that is not polyethylene or one of the alcohols that is used. At one time Avtex was talking about putting a sizing on that would come off during the carbonization cycle. You don't care how it comes off as

Pinoli To me that is acceptable, but I can't speak for the carbonizers.

Johnson I don't see that they would care one way or the other as long as we put it through. As long as you can put it through without going through this particular wash cycle.

Beckley If it turns out that there are three of them and one is carbonizable with no removal, it will be better than the two that washing and drying and additional handling. For a period of time, there is some development effort needed to find the best animal.

Pinoli Let me restate my question again so that everyone is clear on it. Myles, would you be prepared to work with a team that is put together to address this issue in open forum.

Towne I don't think, Pat, there is any problem in the development of a sizing that does not need removal.

Pinoli That is not my question. Will Amoco participate in this program without proprietary constraints?

Towne Yes, we'll participate, but let me add a qualifier. If that is the kind of solution we are looking at, I don't think there is any problem. If it can be proven that it doesn't affect the final product. If it has to be removed, then there may be proprietary aspects to the removal of that which might give one of the three of us an advantage and that might be a little bit of a problem.

Thomas If it is water soluble, how can it be proprietary?

Towne If it is water soluble, that might be okay.

Beckley Jim, just as an example, I think this is reasonably appropriate. The removal of the sodium that is in the rayon as a washing step certainly is done differently at all three suppliers with different degrees of efficacy coming from a result of the process and result of their washing. I would suspect that if you give all three of us the same water soluble sizing and you have a detection means that is adequate to determine, we will all end up with slightly different degrees of the amount coming due to the equipment we will be using.

Drake I don't know if I am reading it right, but I guess at the beginning of the program, you really don't care what the rayon supplier uses for sizing, but I would hope that it would not change, once you have gone through the characterization and qualification, without a pre-approval of changing it.

Pinoli That is the point I was going to make to Myles. I think a situation currently exists that you can't change the material that is being applied by North American without prior approval. Unfortunately we are extending specification control back to that level, whether we like it or not. If you think there is an advantage, or some edge, to Amoco downstream, you will never get that advantage incorporated by Amoco unless there is some sponsorship.

Towne Are you going to tell us how to remove it.

Pinoli What I am saying is that a committee can be put together to address this issue and if you want to participate, it will have to be on a non-proprietary basis.

Towne I have no problem.

Pinoli Don?

Beckley If the first question is will we cooperate, answer is yes.

Pinoli Tom?

Paral Certainly.

Pinoli Wayne?

Johnson I just want to make one comment. It seems to me that you have two possibilities. One, if you could take it off without washing, that would be the best thing. It would save everybody time and hassle. That is what they have to determine. As far as analyzing where you are going, it seems to me the first priority ought to be can you develop and secondly if that doesn't work, if North American in all their brilliance, if somebody calls and says hey, I have a candidate, there are ways you can test that. When you talk about a sponsor, I get a little concerned that they are looking for a new space shuttle project. I think that this could be done in some preliminary stages with very little expense and not a lot of hassle and move along. If that doesn't appear to be a viable approach, then I don't know. Then the next one is, can you get it off with something that doesn't have any ecological problems?

Pinoli The answer to the original question is yes you would cooperate. Bob?

Looney Yes.

Pinoli The reason I say it has to be sponsored. If we put a package together and you do this independent work and all of a sudden you say to NASA, we think we have a better sizing. NASA is going to say prove it, we haven't seen it, we haven't followed it and the same thing would go for the Air Force, the Navy. You need a sponsor, somebody that will look over your shoulder and be aware of what is being done, the objective of the program, and the results. ASRM is a perfect candidate at the present time.

Let's just hold the other two issues until after lunch.

Pinoli

We request that all presenters leave a copy of presentation matter with Bill Hall or the secretary so that it can be incorporated into the final report that comes out of this meeting. If you have a clean copy, now is the time to drop it off. If you don't have a clean copy, just remember, when you get back to the office, to put it together and submit it. Otherwise we could lose some good information that could get into the report.

Now I am going to shift a little bit out of context. Rather than go into the oxidation mass loss testing, I would like to address an industry standard for shelf life limit on prepregs. This is an issue that Ed Mills brought up for CSD. Ed will talk about this a little bit and let you know what his concern is and then we will see where we need to go on this subject.

Mills

This time I am going to take the opposite position, the position that everything is the same, or should be. Everyone knows who I am. I am the loudmouth. Basically, what I have found in my experience over the last several years is that we have a plethora of specifications for carbon-phenolic. Actually the same is true for silica and graphite, but the work that Aerojet did about 3 years ago has told us that the carbon phenolic material is more critical. This is not just CSD, I have also done a quick survey of Thiokol, Hercules, and Aerojet, although very limited. I have found that there are four common storage conditions, all of which have a six month life as certified from the prepreggers. The most common are the 40-50°F storage with humidity control and that sort of thing. The total life and retest provisions, this is what I would like to standardize, are what bothers me the most. I have got one program that requires retest even within the initial six months at sixty day intervals from acceptance. I have got a more common use that allows a single three month extension to a nine month total and I have another one that allows 24 months total in with three 6 month extensions. There is also a variation in what I do for the acceptance criteria, as well as the retest. It ranges from flow and vols and only to some of the earlier programs which have IRPI, TACK test, etc., and some of the more recent programs that had physical properties, in particular, interlaminar shear. This is one, at CSD, we are very interested in. The point being basically that there are so many variations that we would prefer to have a generic specification for carbon-phenolic, such that we could interchange it between programs very easily, such that we could order it more easily, and not have to worry about different tests for different programs.

We would like to have the maximum life at and the minimum constraints that is consistent with making "good" hardware. We had a little discussion this morning and around the lunch table about what is good hardware. Good hardware is not just hardware that meets the specs. It is hardware that performs. We need to tailor our specs as best we can to address what those parameters are, but without getting into

constraints of things that don't mean anything, or that the test is not meaningful for reason that someone does it at 650°C and someone does it at 950°C. We need to standardize, which is the underlying thing that Pat has driven home to us over these months.

I have problems that I have seen in our experience with materials that have passed retest which have been unable to wrap due to lack of tack, which have failed to knit. if you will, on lamination, low density indications, which are in many cases related to that if I dissect the part, to a fall-off in interlaminar shear. I do test panels with many parts and I see that one resin system has a down trend of about 20 months and the other one is flat to about 20 months. I won't say which resin system is which because, frankly, I don't remember. I intended to have that all compiled and I will put that together in a package and attach it with a questionnaire for Pat to send out to you in the next month or so.

What I would like to get your input on is your experience, data base, and recommendations for the initial acceptance test, for storage conditions. My personal favorite for this would be something like a 40-50°, 6-month, or 0°, 2-years, although I will entertain input and hopefully we can agree upon something that is consistent with the material and consistent with as many programs as possible in the extension periods and requirements and that is really all, that is my soapbox for now. I am sorry that I didn't get a chance to put this together in a little bit more formal way and the questionnaire, but I will get that out in the next month. Any comments, shoot at me now while you have the chance.

Denault

I have a comment on the storage conditions and I know what some of your specs say, but my experience has been that yes, you are supposed to store it at 40, you can bring it out and let it sit on the floor for a month at 90° and this has happened. Not intentionally, but that is the way the weather is.

Mills

There is one other point that I should have made, but didn't, in my haste. A lot of specifications have maximum requirements on out time. Again that is something Aerojet showed us, that the 5055 at 7 days at 70°, I believe it was, was where you started seeing changes. If you went up to 104°, then one day was sufficient to cause you to have advancement of resin system. Presumably that would be fairly broad, in terms of this application. So yes, that would be another thing that I will mark on my copy and include in the questionnaire, in terms of limits on out time. IUS for example, has a thirty day limit between taking it out and cure and it has, I believe, 80° with a set provision for single excursion to 100°, not to exceed 24 hours. It is very complicated and I would like to simplify it, but we do recognize that concern.

Ismail I don't remember that you mentioned anything about the atmosphere of storage. To me that would be as important as your temperature of storage. Now regarding the temperature, it seems to me that you like the storage at 40-50, what is wrong going to lower temperature because eventually, the lower the temperature, the lower the reaction rates would be, whatever those reactions are. Secondly, why didn't you mention something about storing it under inert gas, like helium, rather than air where you have the stability of oxidation?

Mills In answer to the question about storing it in an inert atmosphere, that is obviously very costly. What we normally do, is require that it be in sealed bags with desiccant. We are concerned about storage and moisture pick-up, that is definitely a concern. Temperature, we would prefer to store at 0°F, but that requires freezers, and normally most of the users do not have freezers. They have refrigeration capability, which is typically below 50°F. I would prefer below 40°F, but below 50°F is a reasonable criteria, rather than an absolute. I don't want to generate a whole bunch of NCR's at 43° or 41° or something like that when my typical capability that is common in industry is 40°F to 50°F.

Drake Looking at it from the fabricator's standpoint, what one fabricator would think would be perfect for processing, another one would say that it is much too old and dry. It depends upon the fabricator's process and not on the age of the material. If you can get it into the part configuration, any one of the phenolics will make a good part even after having been set out in the sun for years.

Mills I am not sure I agree with that last statement. We have seen some fall-off in interlaminar shear properties that is fairly dramatic at two years. And that is 2 years stored at 0°F.

Drake Hitco makes brakes and they have material that 3 years old and been stored...

Mills Flat laminates are obviously easier to make the tape wrap, straight tapes are easier to make than bias, because bias, you are typically trying to make them into a shape. That is not to say that between IUS and D-5 and whatever happens to be common, in terms of basic geometry, that the requirements shouldn't be the same. They aren't right now. I would like to keep it simple and probably take the conservative approach as to what will wrap either a bias tape or a straight tape or a rosette and set that, rather than have two separate or three separate tiers of what is acceptable. I'll look for whatever input I get from the fabricators and will try to coordinate that and see if we can get a happy medium. Maybe we won't reach one, but obviously it is desirable to have a single generic product as much as possible. In the real world, the manufacturers cost transfer material from program to program. They may buy it against one program, and cost transfer it to another program within the

accounting system. I am faced with the problem of certification to multiple specs or recertification, which is expensive and time-consuming. My goal, I guess, is a mil-std, phenolic spec which is a pipe dream probably, I'll admit. I would like to take a shot and see how close I can get.

Larson You may consider having various levels of storage conditions. In other words, level 1 would be this temperature and level 2, another one, depending on the requirements of the program.

Mills That would certainly be a valid point. That is the sort of input I am looking for.

Golde Ed, currently Thiokol is doing some testing to clarify a storage temperature issue relative to advancement of resins and so forth. I might offer that you might get in touch with someone in our design group. I would like to go back to some of the comments Ken made. We are at the point now in the shuttle program where uncertain components, we restrict the use of one versus the other strictly because of processability as far as diameter and wrapping it. We had initiated some efforts with NASA to change resin to filler ratio that we felt would have made both of those materials very close in their applicability. Unfortunately we couldn't, and that has been dropped. We hope to pick it back up within 6 months to a year.

Mills I would appreciate what data you have that you could make available and the same with Aerojet, because I know that they did some work in 87 that was more toward out time and parameters, lay-up parameters as it affects usability, but clearly everyone of us in industry is going off and trying to kill the same snake in slightly different ways. It is a problem for all of us and it is going to continue to be.

Bhe I have a question for Rick. You are looking at both 91LD and SC1008?

Golde That is right.

Bhe They probably have different reactivity.

Golde We are addressing both of those.

Bhe The other thing that is on paper, I guess, you could also vary the temperature of the nozzle with your tape wrap process.

Mills You mean alter the temperature to compensate for the age of the material?

Bhe Well you have tolerance, right? The temperature of the nozzle. You have to make it, you have to pack it. If you don't pack it, you have to strip it.

Mills Well, giving the processor the amount of flexibility he has now, I can still create a part that processes completely and when I get it out, I either have low interlaminar shear or I have excessive LDI's. When I section the part, I find that the resin did not flow properly and I make the assumption that since it passed the flow and vols, although it was high on both flow and vols, that the reason it passed was because it was moisture rich rather than being real flow. But that is an assumption. Obviously, we need to do some homework as well as solicit input from those that others that have tread this path. Thank you.

Pinoli This subject will go under advisement and Ed will be in contact with a lot of the membership. We will see if we can move this through the committee and see if a consensus exists to address this issue.

I want to now go briefly to Advisement Task 2, which is fabric oxidation mass loss testing. Myles has some new data he wants to bring in and show; then I will talk very briefly about some old data that complements some of the work that Ismail was talking about this morning. Then I want to move quickly on to the silicone contamination update with Tom Bhe. So Myles, do you want to take the podium?

Towne If you recall, we started out on this task with a TGA system which on round robin was not found to be reproducible between different laboratories and beyond that, it appeared that the frequency of the testing that would be required to do a good job on this was so high that a more rapid determination was needed, something that could handle production a little better. I have talked at a couple of the previous meetings about so-called rapid oxidation tests. What you do is just expose fabric samples in an oven to circulating air at 375°C. Obviously some of the questions that arise are the container in which you put the sample and what effect that has on the exposure of the sample.

At the last meeting I gave some data. It was on the more oxidation resistant fibers that were used primarily in polyamide-type applications. We compared the system that we had been using in Parma in which we suspended the sample on a paper clip in an oven, with circulating air around it, versus a test that NASA-Lewis had recommended in which the sample was placed in a petri dish exposed that way versus an ASTM test which had been originally developed by Celanese in which the sample was placed in a beaker, 150 ml beaker. On the long term test, on these more oxidation resistant materials, and I am talking long term, 500, 1000, 2000 hours, we did not see a great difference between the methods of exposure. In this case, we are talking about something that has to be done much more quickly, with higher oxidation rates, so you might guess that the exposure conditions would be more significant than in the long term test. This first view graph that I want to put up is one I did have last time. I was comparing in this test at 375°C with rapid movement

of air around the sample, the suspended sample on a paper clip versus a sample that was laid down on a petri dish. The samples were about 1 gram and the petri dish that we used was 100x20 mm. It is a convenient size to handle. You can pick it up with forceps quite easily and I thought that would be a reasonable test. Of course you have to remember when you are looking at these materials, the lower fired rayons, in particular, that they do pick up water rapidly, so any measurements that have to be made, have to be made very quickly. If you wait a few seconds, in fact, you can see the balance moving. It is a question of getting rapid measurements. In the petri dishes, in this test, I had removed the sample from the dish and placed it in a desiccator until I was able to make the measurement and I did a study of how many seconds it took for each operation to get an idea of how much moisture I was picking up. To compare the two methods, I performed both 4 hour and 21 hour exposures on materials that included some of our own VCL made from North American Rayon and some 1983 version North Hollywood material. In the suspended case, the 4 hour test matched up reasonably well with the petri dish, for the VCL, 3.8 versus 2.74 and in the 21 hour, 16.83 versus 14.72. In each case, a slight reduction when it was in a petri dish versus suspended air. This wasn't greatly disturbing, but perhaps about what we expected.

In the case of the North Hollywood material, we had a pretty good weight loss here, similar to what we have seen before. In the two cases, again a slightly greater weight loss in the suspended specimen versus the petri dish. In our discussions earlier, it seemed like a petri dish method would be a lot easier way to handle this than depending on a group of operators to weigh the samples suspended in air while maintaining the same time period between taking it out of the oven and getting the weight. This looked like it was a good idea. The samples that I did in petri dishes here, I put in a desiccator. Pat and I talked later, it would probably be easier to cover the petri dish. This is the data I presented last time.

Denault You lost 100% of your carbon?
Towne Yes, it disappears.

Denault At 375?

Towne Yes, very definitely. Okay now, to update you on where I have been since then. I have some other test data here now. This was trying to refine the test with the idea that we wanted to submit something to a round robin and I used this time a petri dish that was 100x20 mm, keeping it covered, not putting it in a desiccator. When I talked to our lab people in Fostoria, they said, that is nice, but even a petri dish is not sealed tightly and you can't depend every operator to do it the same way each time. It may sit around for a while, so it would be better if you had it in a weighing bottle, which was pretty well-sealed. I took that recommendation and looked at

possible weighing bottles for doing it. I picked out two weighing bottles, I call one a tall and the other a low. The tall is 40 mm ID by 80 mm high. Now I gave Pat the Kimax ID numbers on these. They both have the outside cover so you are not going to disturb the sample by pushing a cover that fits inside.

Denault You still have ground glass joints?

Towne It is a ground glass joint that fits on the outside. That was the case for both of these. You don't disturb your sample. The tall one weighs about 75 grams, the low one weighs about 107 grams. This might make a difference if you have a balance with a 100 gram capacity. I had to use a different scale for measuring this in our lab.

Pinoli Balance, please.

Towne Balance, yes. That might make a difference. In these cases, you are weighing a covered sample, so you take the sample out of the oven and cover it immediately. You have your covers matched up with your bottles, so when you put the cover back on, you obviously get the same cover, you have to let it cool. In the case of the petri dish, you are taking the sample out of the petri dish and it cools to room temperature almost instantaneously. You don't have to worry much about the effect of temperature. With these bottles you do have to wait for the bottles to cool, because they are going to suck in some air. It is significant. If you bring it out at 375°C into the atmosphere for this bottle, I calculated you are probably going to pick up 80 milligrams of air during cool-down. That is a very significant effect on the weight. You do have to let it cool. That air that is sucked in also contains moisture but that weight is down in the insignificant range.

Looking at the results, I was in a hurry and I did not get the temperature of my furnace stabilized at 375°C but for what I was doing 382°C was not that different and I wanted to get it done that day, so I left it at 382°C. The samples I used were a little larger than I used the last time, 1½-2 grams. I think this is rather interesting, the way the results came out. For the North Hollywood material, the exposure time was 3 3/4 hours and I did not get good reproducibility at all. Now this may be sampling, but that was disturbing. In the case of the VCL, it was reasonable. Somewhat higher than I had in the test I showed before, but I think that is accounted for by the higher temperature. Again, for the North Hollywood material, 100% weight loss. The sample disappeared and this of course was sitting uncovered in the petri dish. The results are consistent. You will note that in each of these cases, the highest test here is the highest test here. I recorded the position in the furnace for each of these samples and put them on two shelves and let's see, I have 18 samples. I had nine on the top shelf and nine on the bottom. I recorded these positions on the shelf, front to back and side to side. In a sensitivity study, I was not able to get any

significant difference by position except where these North Hollywood samples happen to be. They were so far apart that they upset the whole apple cart. Otherwise, there did not seem to be a significant effect from the position in the furnace.

Looking first at the tall bottle which we would assume would confine the sample and protect it better from the atmosphere. In this case, the weight loss went up from what it did in the petri dish. For the VCL, the same thing happened. Again with reasonable consistency and again the same relation with all samples. Going to the lower form weighing bottle where you had additional exposure to the atmosphere, the numbers again in both cases went up. I think we are definitely seeing an effect of exposure in the kind of container as we had seen in the hanging sample versus the sample in the petri dish. The thing that was surprising is that the petri dish sample which should have the maximum exposure to the atmosphere gave the smallest weight loss.

Ismail How did you have your sample in bottle? Was it standing up like this, or laying flat?

Towne In the tall weighing bottle, I put a coil in so it was standing up. In the case of the petri dish, in every case, it was laying down. In the case of the low bottle, some were each way. I tried to coil some without having the sample stick out of the bottle. In other cases I rolled it and laid it flat in the dish. There is an effect of the proximity of the sample to the bottom of the container. This is what I think is probably the reason for the lower results in the petri dish. When lying flat, the bottom part of the sample is not exposed very well. In the case of the tall weighing bottle, which you see gave the most reproducible results, you are forced into doing it in a coil and it all has the motion of the air around it to give it the more uniform exposure. In the case of the low bottle, of course with North Hollywood material, I wasn't in a position of being able to tell which way I put it. Did I put it in a roll or did I put it in a coil? I wasn't aware of that problem at the time I made the samples, so I am not sure what happened. In these cases, this one happened to be in a roll lying flat and these others were coiled.

Drake What was the significance of North Hollywood versus VCL?

Towne The North Hollywood is that high sodium material that Ismail was talking about. That is the STS8A-type material.

Pinoli That is 2400 ppm +.

Towne Yes. As I look at the results here, I guess my recommendation would be that the tall weighing bottle might be the type of container that would give you the most reproducible results. The petri dish depends somewhat on the size of the sample. I think in the earlier test where I used a smaller sample, 1 gram, they were lying flat on the bottom. In this case they were curved up on the edges some, so it was somewhat different exposure in the petri dish this time from the previous test I did. This tall bottle forces you into doing a coil and it forces you into a coil that is approximately 3 inches by some other dimension, maybe 5. I think that would be something that you would standardize. It is an easy test to do in that kind of bottle. You take it out and cover it up with the matching cover, cool it and then weigh the bottle with the sample in it. You have restricted the ingress of moisture. So my recommendation at this point is I would like to see a round robin at least using the tall weighing bottle.

Hemmelman Myles, were your samples all pre-dried?

Towne Yes, all pre-dried.

Hemmelman In divisions?

Towne Yes.

Pinoli Would you recommend 4 hours or do you think we have to go to 20 hours?

Towne I think 4 hours is sufficient.

Pinoli I agree.

Towne Four hours you can do in a day, certainly.

Ismail I have a difference of opinion about using bottles versus petri dishes. I think I agree with all your statements, but if you had tried to flip over your sample every 30 minutes, you will get beautiful, consistent results. I tried that. When you put it in a petri dish, flat and leave it there, obviously you are oxidizing the top and probably not much in the bottom. Whereas if you keep flipping it like a hamburger every thirty minutes, you will get excellent weight loss which is much better than putting it in a bottle because when you put it in a bottle, you are right away creating a concentration gradient inside your bottle for oxygen. Oxygen will react more at the top and less and less down there, so the concentration of oxygen here would be higher now that the bottle is zero and now you have your product gases coming in from opposite direction so you are creating some current.

Towne I agree with you, Ismail. I think that this offers the possibility for doing a nice scientific piece of work, but I don't think we can depend upon operators and production laboratory to do what we need to do to get those consistent results.

Ismail How do you expect me to coil it the same way that you coil it?

Towne It will uncoil to fill the size of the bottle. This is the reasons why I think this is the appropriate one for a laboratory. We know that everything that can possibly happen will happen. It will contain the sample reproducibly from time to time. I think any coil I took that was 3 inches by whatever, across the width, would uncoil to the same degree within that bottle.

Bhe Myles, what's the rationale for 3 1/4 hours more than the first one?

Towne 3/4 hours more. I was trying to get reproducible results so I wasn't concerned about duplicating what I had done before. I was in a hurry, that is why the temperature is up. These things, I know are different than what I did before. I was trying to get these out in a day and that is what my schedule allowed.

Denault So you pre-dried the samples at a temperature.

Towne Yes. I pre-dried them at 110°C in a vacuum oven.

Denault And the glassware, also.

Towne Yes. In the case of the petri dishes, I took the samples out and weighed them in the air so there was that little concern about the pickup of moisture in the weighing operation. In the case of the others, I just let them cool.

Pinoli I would like to comment for people like Ismail who weren't present at our last couple of meetings. This particular test is designed to be a go, or no go test. It is not really designed to be a scientific test. What the industry is looking for is a relatively short test in which they can subject their fabric to see if it is highly sensitive to oxidation. We have done all the sophisticated TGA work. We have looked at activation energies, we have looked at the relationship with sodium to the reaction rate. We have all of the data as background. Now we are trying to reduce this to a very simple test that the manufacturer can use to screen good versus bad fiber. Now when I look at the data presented here, we are trying discriminate something like 10B fabric that essentially disappeared in 20 hours versus 15% for conventional fabric. That is a strong discriminate. Likewise, the difference at 4 hours between those two products is 31% versus 4%. I think this is enough variance between the performance of those two products that the standard deviation of the test procedure

itself isn't that important, i.e. $\pm 10.3\%$. So I will propose at this point that Myles and I work on reducing this into a standard test procedure and get it out to all the carbonizers. What I will do, is send the weighing bottles with samples out to each one of the test laboratories and have them perform the test independently, reporting the results back at the next meeting.

Bhe Are you going to characterize the bottle?

Pinoli I will look into that issue.

Armour Is fabric oxidation mass loss part of anybody's specification?

Pinoli It was part of the RSRM specification as an engineering test.

Armour That was just to screen for sodium, high sodium content?

Pinoli The intent was to screen out the product called 10B, a variation that we found would support combustion.

Armour Will this test do that?

Pinoli Yes. This test will do that.

Armour From a material that meets the spec versus a material that is slightly over the spec in sodium content? I don't think so.

Pinoli Now that we have introduced a sodium level into the RSRM specifications, the likelihood of us getting something like this product into the system is fairly remote. There is still a possibility. That gets into another piece of data. Maybe I should show you this.

DiMeo Did you say this test was in the RSRM spec?

Pinoli Yes. It was in the RSRM spec as an engineering test only.

Hemmelman It hasn't been there for a long time.

Pinoli Yes, we dropped it out about a year and a half ago. The reason that we pulled it out was the we saw so much variation in the test results that we had to pull it. I just want to quickly cover what Bill was talking about. What we have done in the past is develop reaction rate kinetics data on various rayon fabrics that could be introduced into the program. We were really interested in studying experimental

10B. We have used the arrhenious equation and plotted oxidation rate versus temperature. This is mass loss rate versus $1/T$ temperature, now you can compare the performance of any of these products like 10B and this line here is the same product 10B after it has been water washed. In this case we have taken out the majority of the sodium and reduced it from 2400 ppm to 1000 ppm. We have heat treated that same fiber to a much higher temperature now, going all the way to WCA. What you can do now is put parallel lines here showing the effect of various heat treat temperatures. If we are talking about ASRM material, a line would fall somewhere around in here. Now if we are holding at any specific temperature, say 400°C, drop down and reference the rate. Likewise, you can see that if you water wash that product, the oxidation rate drops off dramatically. Also if you fire the material to much higher temperatures, the oxidation behavior changes dramatically. There are two strong drivers with regard to the oxidation rate. One is the sodium level, the second is the firing temperature of the fiber. Your question, Bill, was why do we need this? If we reduce the firing temperature of this fabric, and even with the low sodium level, you could still have a very high oxidation rate. Are we going to see high oxidation rate on ASRM?

Ismail How did you measure your oxidation weight?

Pinoli TGA. These plots represent at least 5 isothermal runs per each variation.

Ismail Here is a technical question for you, Pat. You are talking about oxidation rates and weight loss rates, assuming that they are both the same. I don't think you are right.

Pinoli We have chemisorption and mass loss. I have assumed chemisorption is relatively small compared to the mass loss.

Ismail No, I am not talking about pre-zone 1 where the temperature is much higher, but I am talking about the low temperature where you have two processors and you are assigning the net weight loss as

Pinoli We are going to be here all day on this issue. I have to move on. I am sorry. Tom, do you want to talk a little bit about the silicone contamination at Aerojet? Maybe Don will want to talk a little bit. I would like to limit this to about 10-15 minutes. Then we have to move on to the Expert Systems and allow them ample time to present their results.

Bhe For some of you that are not familiar with what is going on in the last, I guess it's the beginning of October, I will give you a little bit of background. Basically on October 5, this year, PK second stage nose cap fabricated from US Poly, carbon-phenolics show signs of oil, spotting or something. This oil is weeping from the

splice thread location. On October 8, BP confirmed with the thread supplier and informed us that the thread lot received in April of this year and used until October 5, contained, one of the lot contained 21% by weight of silicone lubrication. On October 30, carbon-phenolic produced in November of 1989 that is used in small ICBM second stage nozzle exit cone was tested positive for silicone contamination. This kind of put the suspect period from June of 89 to October of 1990. By testing of the retained sample, BP or US Poly, they have been able to identify which lot was okay, which means no lubrication, silicone. This carbon-phenolic prepreg bias tape used for the PK and small ICBM nozzle application contained approximately 24 splices of bias tape in the spool. Each splice is butt joined and sewed in zigzag stitch using the nylon thread. Nylon fiber is produced by DuPont and processed by a Synthetic Thread Company into thread by applying "producer finish" which as far as we know is vegetable oil based. It has a low percentage of this oil. The purpose is to allow the addition of twist and ply to process the thread. No silicon oil is used in this producers finish. This no lube requirement for the carbon-phenolics prepreg application is stated in BP's verbal and confirming purchase order with Synthetic Thread. The Synthetic Thread also provides the same nylon thread with varying amounts of the silicon oil lubrication for the garment industry. This is basically what the background is.

Right now the efforts undergoing in conjunction with BP and also TRW is to clean up the silicon contamination at BP Chemical prepreg sewing and slitting facilities and also in Aerojet, the tape wrapping building. Basically we disassemble the roller from the equipment. You soak it in acetone.

Denault Acetone?

Bhe Yes.

Denault That wouldn't do it.

Bhe That won't do it? Well, to remove the silicon contamination. Also other contact surfaces that cannot be disassembled, we wipe with acetone and the verification of the cleanup was done by, well, we call it Aerojet recommended procedure approved by TRW and it is basically using FTIR, the infrared scanning.

Denault On the wash.

Bhe On the wash, yes. Then we do a cotton swab on the surface of the equipment that has been cleaned. On the cotton swab, we basically take about 10 cc of trichloromethane and stick a cotton swab in there and start wiping it, on the roller

and then evaporate it, the solvent, and put it on the KPR palette and run it through the scanner.

Ismail If I understand you right, you are saying that you wash the fiber with something acetone or whatever.

Bhe No, no, not the fiber.

Denault This is the decontamination process.

Bhe We are talking about the rollers.

Ismail But you haven't tested the fiber itself to see if you have silicon left on it or not.

Bhe You cannot. We are looking at the part right now. As far as the suspected silicon oil contamination prepreg material, basically it was scrapped.

Pinoli The whole lot, residual prepreg and parts?

Bhe Suspect that we can trace back to...

Mills You didn't scrap all of it. You went back and traced the material that had the thread in it. Can you also extract the piece of thread from a roll of cloth and test?

Bhe Yes, we are doing that and in fact, I think it was last Friday, we brought back that spool of thread that doesn't have the finish and spool that does have the silicon oil finish in it. We are doing testing.

Mills I am talking about taking a roll of prepreg that is out on the floor that is suspect because it is in that time frame and peeling out one of the joints.

Bhe We did that, too.

Mills Are you satisfied with that as a means of clearing that roll of tape, if it tests negative?

Bhe If it tests negative, yes. The hardware fabricated with the reported discrepant material, right now we are still in the process of identifying those and the hardware that has visible silicon oil blotching and spotting was scrapped. We also, that same equipment that was used to wrap the first stage Titan liquid engine, which is a silicon-phenolic base and we identified this hardware and we consider it a secondary contamination. That is after you tape wrap the nose cap material which has the

silicon oil and the operator is supposed to clean the roller and the equipment prior to each wrap. Now assuming that they did not do that, you might have possible contamination, but we identified those right now and we did look at mechanical property on the forward and aft end specimen. We are also doing this FTIR and cotton swab test. The work is still going on right now.

Schmidt Tom, I didn't understand. What is the source of the silicon oil.

Bhe The source is stitching thread.

Pinoli Don, would you like to make a few comments?

Beckley I had rather not, but I will. The kind of background that I can give you, I think Tom was pretty accurate in everything he said. We learned about weeping in hardware back in the 60's, 61, 62, 63. Heat shields showed up with weeping marks on them and we basically learned to write a thread spec and the thread spec was based upon a max allowable extractable. At that time, he mentioned, the finish was hydrogenated petroleum vegetable oil, Crisco. You could say this, the thread won't go through a sewing machine without a lubricant on it, so you are going to have something on it. If you don't have a lubricant, what you get is producers finish, which is what DuPont puts on their fiber so they can make nylon and a thread maker can twist and ply it without the filaments breaking and so a sewing machine will take the material. Once again, the amount that DuPont puts on is $1 \pm \frac{1}{2}$, so once again a relatively low level of lube. Back in the 60's we had this 2% maximum allowable extractable, bought material for years from this thread source, bought it reliably, they had a process deviation that said anytime the material comes in from USP, make sure it contains no lube and the reason for this is other sewing operations require far more lube than 2%, so we are really in a restrictive end of a specially used material. They put on in about 6 steps up to 20% lube. Most of it is silicon. There are some other ingredients in the system, much like the finishes we were talking about this morning, but it is primarily silicon. The particular instance that happened-we called for a thread lot. We called in with essentially a new buyer and she either didn't ask for no lube thread or the man who received the order, who has been receiving our orders for 20 years, didn't recognize the BP Chemicals was old US Polymeric. So he thought he had a new girl friend on the phone and a new company, and by the way, they could use some thread they had some stock because we wanted it early and he had this thread in stock, so in two days packaged it up and sent it to us. We had been purchasing the thread on a regular statistical sampling plan and it had gotten down to the point of buying it on the surface. That is the finish was acceptable and what that turns out to mean to them is that if the purchase order specifies 20% and you have 20% on it then that is a pass. When the certs said pass, he thought it meant 20 and we thought it meant none. That is the genesis of the start of it. I

think the thing that gets worse after that is when they read our purchase order, they approved it, which said no lube, which says something about how you conduct your business. Do you read the purchase order that comes in after you have had your telephone call? The first thing is there were a number of months between the receipt in April and the discovery by Aerojet in October that we weren't informed of the situation or it could have been rectified. That is the background.

A few more things to add from the situation. We have occasion now to study the extent of the migration of the silicon and maybe some of the things that would help to understand about it. We contacted the silicon supplier which in this case is DOW Corning. DOW said that the material being used is completely soluble in ketones, hence the reason for the cleanup in ketones or completely soluble in xylene or toluene, also acceptable for cleanup, slightly soluble in alcohol. It turns out it is a fairly short-chain, low molecular weight silicon, so that is one of the better things going for it. It is relatively feasible to clean it up. The inspection technique that Aerojet came up with and that we have been using since then is with FTIR and we have the sensitivity level down to 6 micrograms that is detectable. It is probably detectable at 3 or 2 millionths of a gram, so we are detecting a tiny amount of silicon and one of the incidents that showed up is this potential extension of the date back beyond the April receipt of thread and several of us suspect that that is merely a silicon atom that has gotten into the system and probably didn't come from the thread. We know how to detect it, we have learned how to clean up the equipment. We have probably have spent on some of our sewing machines 5 cleanups, but it turns out that what was really going on is that if you have a little leftover silicon and you touch it with a clean rag and then you take that rag and dip it back in more fresh solvent, you have now contaminated that and you can chase this thing around forever. We divided each of the sewing machine areas up into 5 zones and we would take the set of rags and the set of solvent, clean that and set it aside. Then take the next area and clean it. As soon as we used the cleanup procedure, the ability to demonstrate the equipment was clean was 100%. There are 4 bands that show up in FTIR at this sensitivity level, so it is a nice easy identification beyond this quantification of 6 micrograms, it is difficult to quantify. Thread can be pulled from a seam as you asked Ed and you can extract the thread in acetone and effectively get a signature as a means of confirming whether this thread is one of the contaminated lots or not.

The next thing that we did that I think is significant. We laminated plies of materials, made laminates with the same lot of prepreg with silicon thread known to contain the lube and known not. We ran tensile, flex compression, and flat wise tensile where you are pulling the specimens apart. One of our customers ran another series and they ran shears. In both cases on 5055, the difference in numbers mostly favored the siliconized thread in terms of the structural values.

The next thing that we have done is to use the Samedax(?) to look for the extent of the propagation of the silicon and I made some laminates which were essentially 3 plies thick, a sewn joint, a butt joint seam, a cap sheet top and bottom, laminated them along enough with a 7% flow to get it to knit together and then peel them apart, so that we could look at these basically virgin surfaces. What we saw was an extent of migration typically less than 200 thousandths from the center line of the thread in the thread ply. In the cap sheet above it, about 100 thousandths in width, but the ability to penetrate through a cap sheet and come out on top of the next layer, so it does penetrate vertically pretty well when you laminate with a compressive force down and flow the silicon out. We had an opportunity to look at some finished hardware that was, incidentally, I didn't say this and Tom didn't either, what your eye visually sees is a weeping mark, an oil stain around the end where the thread comes out against the machine surface. That cut end wicks the silicon lube at the concentration that is there onto the edge of the part. In the re-entry heat shield back in the 60's, this weeping would go on and they would wipe it with acetone and it would go on and they would wipe it and finally they had flown a bunch of those shields, so we were somewhat aware that there was some evidence of a problem from that end. The mechanicals that were run by Reinhold and our mechanicals said that because of the relatively small concentration, the numbers are something like a pound of lube which is .8 of a pound of silicon in 2700 lbs. of prepreg. So you really have a highly dispersed system.

The next thing we did on this finish part with the cut ends. We took the Samedax and looked down along the thread and in that case got a very nice, perfect replica of the fact that the silicone is all right in the thread pouch in the threads themselves, but hasn't migrated outside of that in any direction. Ultrasonic shows no effect, x-ray shows no effect, microcracking shows no effect, so we really have at this point yet to see anything other than the visual contamination event. We have documented now at least 5 firings with the known thread and no perceptible effect on the firing. There have been 3 and SICBM and there has been one on a PAN program. Out at Hercules there have been a Mark 104 and the general indication is that it is something we should be concerned about and corrective actions have been put in to go back and run extractable on thread and evaluate the thread so it doesn't happen again and to effectively work with our customers. There are 7 involved programs that we are aware of and either 4 or 5 at this point have decided that it is business as usual.

Drake

Can you list the programs?

Beckley

There is the MLV Delta and Titan 4U. That in my mind is really two programs. There is Peacekeeper 2, Mark 104, Star. The SPIP program is six. The seventh is SICBM.

Bhe Don, in your testing did you use the 20%?

Beckley Yes, we used the contaminated thread lot. It is 21% based on the thread rate that is effectively the amount of lube that is on that lot.

That is about the extent of it, except for one more set of data. It was pointed out that when you do Samedax you penetrate up to 50 angstroms deep and there is concern that there may be a very thin lighter layer that the Samedax is not even sensitive to, so we have analysis being run by our Sunberry research laboratories on XPS which will determine the monomolecular layer and by SEMS which will get not only the presence of the thin layer but it will get us whether the form that is there is silicon as an organic polymer in silicone phase or whether it is silicon that comes from the prepreg. We have about 100 ppm Si in the typical carbon-phenolic prepreg. You heard about the big silicon peak that Ismail sees and is there. When we did out Samedax, we established what the background reference level is and then when you move into an area that has an increasing silicon concentration, it goes up by a factor of about 5. In other words, where silicon is it shows up as 5 times more concentrated than the background area. We are waiting for the XPS, SEMS data, now to confirm whether the Samedax was seeing the whole spread picture or not. I think their observation at this point, it depends on the curing technique. Autoclave or hydroclave, which is essentially an isostatic force doesn't permit much migration where as pressed laminate that says put force in this direction and squeeze perpendicular to it, we found an extent of migration that looks like it is a couple of tenths of an inch. Any other questions? That is about as much as I...

Bhe One more thing. After you do the bonding of those three plies, you look under....

Beckley The Samedax is how we look at it.

Bhe The resin, the fiber, the filament?

Beckley In the flat wise tensile, for instance, where we had a seam in the 9 ply laminate. One silicon bonded joint failed on that ply, four didn't. On the unlubed thread, one failed in the thread ply and the other four didn't. There is not much distinction at this point. Structurally there doesn't seem to be an effect that you can find. On the flex specimens, we mounted one on the top surface and one on the bottom, so as to get a either a bumping effect or a tensile effect and it didn't make any difference.

Drake This nylon thread is limited to tape wrap products?

Beckley The purpose of the thread is to put together those 45° strips to make the tape wrap a continuous process.

Drake So any products that use bias tape would be susceptible?

Beckley No, we function with three different threads. We have a nylon thread and it is generally specified as using the government spec, BT295, and the spec says don't put any finish, meaning lube, on the thread unless it is to enhance sewability. The caveat itself would let you have any amount up to 20% by the governing specification. In general, we and our customers have gone to using that government spec rather than staying with the spec we had written which basically had a particular caveat against it. The other two threads involved, there is a black dacron which is a high purity thread for re-entry and there is a white dacron, white polyester which is also a high purity thread for another re-entry application. We function with three different threads.

Drake This would be only the nylon thread?

Beckley The thread lot that is involved in the Aerojet report is nylon thread. We pulled one specimen back from Aerojet thinking it might not be nylon, but it turns out that it is.

Buechler Are you testing both the PANs and the rayons?

Beckley Yes.

Buechler Do you see any difference for whatever reason in terms of migration properties?

Beckley Not so far. The parts at Hitco, Gardena, in composites which are basically deltas at this point are both in rayon and in PAN. They are doing both and they were both done with this nylon thread and they both show weeping and they both show no migration outside the thread itself. In their case they have studied it extensively with ultrasonic and x-ray and can find no difference in the signatures that they are getting.

Pinoli Don, I would like to ask one question. Is BP going to send out an industry alert or are you going to handle it by contacting everybody individually?

Beckley Well, we have contacted all of the customers that are involved. What I have seen is Aerojet has written an industry alert and I don't know if they are going to mail it or not. You handle it in the way that you think best and with 7 customers involved and we are working with each one of them. They are the people involved. It is good for everyone else to know it, but not everyone else has the same problem.

Mills I had understood that there was also some white polyester threads affected. In fact as early 5/89.

Beckley Chapter 2. Once the thread monster got out, we then had to look at all the thread in the system and as it turns out we tracked polyester thread, this is the white stuff, and apparently from our retainers that we have around, 2 polyester thread lots not with 20% finish but with finish levels of 5 and 10 that may have been in the system back many years. I don't have the dates with me right this minute.

Mills The earliest was 5/89.

Beckley I think I have been corrected since then that one of those two lots has now been accounted for with every spool of thread that we got still in house. There may be only one other thread lot involved. We are looking into that and we have notified all of the polyester thread receivers.

Mills The seven programs that you mentioned earlier, are they nylon?

Beckley They are nylon.

Mills Do you have a similar number and names for the polyester thread.

Beckley I am not really up on it. The only additional one that I can think of off hand is Kaiser has received a bunch of it on what effectively, are their programs because they are one of the people that prefer polyester thread.

Mills I can tell you that IUS has two lots and that Intelsat has two lots and the D5 has, suspect lots, and Titan has some suspect material. There may be some other programs that may also have suspect material.

Beckley Kaiser gets attention next week in terms of where they are and what they are finding.

Mills Is the data going to be published shortly on the test results that you have?

Beckley It is available anytime and I am on deck to write a white paper on this.

Mills I guess I would be very interested in seeing any studies on bondability to surfaces that intersect the sewing thread.

Beckley There is a study coming out of Aerojet that they are doing metal to metal bonding with various types of degree so there are studies. Our QA manager came out of Northrup and he had an experience that is kind of interesting that related. He said that in the metal bond area and the adhesive bond area, silicon is just a no-no. You just can't live with it and you say bad news. But in their putting the B2 together, they found out that for composites, it didn't make much difference. In other words,

it, the bond is hardly affected. At least they weren't aware of anything and they took off a bunch of restrictions that they were applying to their metal bond areas for their composite areas. If there is any hope in that area that's it.

Mills I would be interested in bonding to metal because that is what we have to do on several of my programs. Obviously not the carbon, but the silica-phenolic, we bond.

Pinoli Don, we have to move on.

Beckley I am glad to let you move on.

Pinoli Gloria Ma and Peter Kraus are here from the Expert Systems Technology Company to give us some insight into a new NDE piece of equipment that might be of tremendous value for us to look at resin filler fabric content in prepreg and possibly tag end testing and hardware testing. We might be an hour late, but we have finally made it, Gloria. You have the floor.

Ma What I thought I would do is start off by saying a few words about our philosophy and our business concept and then I will go into the operational theory of the instrument and then I will actually show you some data and a summary of the data base that has been established to date at various industry sites, primarily with Fiberite and Hexcel and lastly, to show you a five minute video which actually shows how the instrument operates. I thought it would be better seen than for me to describe it. That is the summary of my talk.

We are focused on developing innovative, non-destructive methods to characterize important properties of advanced materials. We are different from traditional ultrasonics which are basically qualitative measurements, we give you quantitative numbers and we are focused on doing process control, using NDE for process control, versus the traditional NDE techniques which are mostly into flaw detection at the end of the line. We are really focused on characterizing properties, particularly raw materials like prepreg. Initially we're focused on fiber-resin ratio, but we are also currently working on methodologies to characterize flow, fiber wet out, microporosity, and maybe even degree of advancement of prepreg material. The technology is applicable both in the uncured and cured states, but to date we have a large data base in prepreg and I will be showing you a lot of that data.

Our instrumentation, we develop intelligent instrumentation. There is a lot of software in our instrument besides the state-of-the-art sensors that monitors the parameters of interest. The instrument is totally automated. There is a large knowledge-based software both for the data acquisition and data analysis. In the video, you will see that the measurement process is very easy. The operator doesn't

have to sit around, tweak knobs and look at the wave form and make decisions on how to interpret that data. All of the rules are input into the computers, so it takes away operator-to-operator variability. Any of the errors that could be due to human judgement or any of the various experimental errors that could be associated with the current testing methods which is an important aspect for eventually using this in a real-time situation for controlling composition and the processing of these materials. That is basically our business philosophy.

In terms of the operational theory of the technology, our current instrument is called the URA 2000. It stands for the Ultrasonic Resin Analyzer. The operational theory of the URA 2000 is very generic and is really not limited to polymer matrix materials. It basically handles any two-phase heterogeneous mixtures, provided that there is a difference in the ultrasonic propagation characteristics of the two constituent phases. We have some preliminary data on metal matrix material and radar-absorbing material, as well. We haven't really been focused on developing that aspect of the technique. The operational theory is elegantly simple. It is basically assumes that since the ultrasonic velocity and the volume fractions are both functions of modulus and density of the material, there should be a precise and predictable relationship between velocity and volume fractions of the mixtures. The velocity in the mixture, or in this case the composite form, is a function of the velocity of the two constituent phases weighted by the volume fraction of those phases and we took a very pragmatic approach. Rather than a theoretical approach of developing a theoretical model for this relationship and there are probably quite a few models to predict what this relationship is, the URA 2000 actually took a very pragmatic approach of utilizing empirical knowledge gained from calibration specimens to derive this relationship between velocity and volume fractions. This has several advantages. It minimizes the error that could be associated with any deviation from any theoretical model as well as measurement effects. There could be systematic measurement effects that could come in and corrupt the theoretical behavior. Taking a pragmatic approach eliminates that. The software of the URA 2000 and the methodology also uses a statistically large data base in this calibration process so that you could minimize the random error and maximize the accuracy of the measurement.

We set out to design the instrument to measure velocity very accurately and slowness is the inverse of velocity and you see in a lot of our curves we actually plot the inverse of velocity as a function of volume fractions. In order to do that, we have a special design to measure simultaneously, the thickness, and the time of flight, of the ultrasonic wave. The thickness is measured by a different component. It is a linear, optical device and the time of flight is measured by a state-of-the-art digitizer and pulser. Measuring, once you develop this relationship, basically how you derive the relationship is just take a set of samples, composite materials, that ranges the

resin content or fiber content range of interest, making sure that you cover a wide range, because most destructive techniques have a variance of the measurement of $\pm 2\%$ or $\pm 1\%$. If you are dealing with a 4% range, you are hardly going to see any correlation at all, so it is important that you get a wide range to establish a good correlation. Actually doing the measurement on the sample and then subsequently destroying that sample for a destructive analysis to give you the resin content or fiber volume. Once you establish this relationship, this is stored as the knowledge base in the computer and it is very material specific as well as if you cure the same material system, the uncured resin and the cure resin will have different propagation characteristics and the shape of this curve is different. This relationship is now stored in the computer so that subsequently when you are evaluating them, the same material is called up to derive the unknowns.

That is the basic operational theory of any material that has a stable dimension. However, with prepreg material the resin flows and is a technical challenge to try and take a measurement on these materials, because the minute you make contact with the material, you are changing the effective dimension of the material. There are two processes that are going on. You are collapsing the air that is trapped between the various plies or trapped between the resin and the fiber as well if you continue to apply pressure then you lose resin outside of the area of measurement.

Thomas

That correlation coefficient that you showed on the previous slide, is that constant for all thicknesses?

Ma

Yes, for velocity. There is a process by which we standardize a reference point. Let me finish this thought and you will see how we derive those correlation coefficients on the prepreg.

In the prepreg material, here is what I am talking about. This is a typical deformation curve of the prepreg material over 60 seconds at a pressure usually anywhere 100 to about 175 psi. The initial phase is a very rapid deformation phase and that is air collapse. Then there is a second phase which is much slower and that is the resin extrusion. What you want to do is pick a point, in order to compare these materials and plot your correlation curve or derive this relationship accurately, you have to have a reference point. That point we call optimum consolidation as defined by the point where most of the air is squeezed out but you haven't lost much resin to the adjacent area. This point here, this transition point, you could almost see it, visually around this point here, is mathematically derived as a second derivative of the deformation characteristic. Where the acceleration first approached zero is when you have the change of the transition phase between air collapse and resin flow. That is an additional step that happens with the prepreg materials so that you have a standard reference point to compare samples to samples.

Ismail How do you know that you are separating —— completely? How do you know when you compress it, it is air collapse or maybe you have a continuous....

Ma Yes you do have both processes occurring, but the rate at which they occur is very different. If you go back to the last curve, they go on at the same time, but the predominant activity here is air collapse. After that is done the predominant activity is resin flow so your point here, I am not saying that, one excludes the other. As soon as you apply pressure, both occurs. The predominant behavior at this part of the curve is air collapse, where as the predominant behavior here is flow, and if you go further this is compressing fiber as you continue and sometimes that is within the noise level. Sometimes you see the measurements coming back.

We have designed in the next slide this proof of concept experiment to really show the validity of the basic assumptions of whether you could use velocity to measure volume fractions. With composite materials, especially with prepreg, you are changing the dimensions and you also have material property variations. The materials are not uniform due to fiber area weight fluctuations, due to density fluctuations, resin content and a whole bunch of parameters coming in. We designed a synthetic composite to come up with a sort of artificial situation to test the theory. Here we have a sandwich structure of acrylic and steel and you don't have to use a destructive technique to determine volume fractions. Another problem we have is that we have a very precise measurement calibrating to a much less precise destructive technique. You are going to get a lot of scatter on the data. We wanted to get a proof of concept that gets away from the destructive technique. Here you could calculate volume fraction by taking the thickness of the sample multiplied by the area and summing all your fractions. You don't have to use a destructive technique to come up with a calibration relationship. There are two things we wanted to test in this experiment here. Are we measuring through thickness, an average volume fraction, or are we measuring some surface phenomenon. Here if you have a surface phenomenon, these two will not be the same where as if you have an averaging effect these two will be the same. The other thing is what kind of relationship, do we get a good calibration relationship by taking a look at velocity through this material as a function of volume fractions. This is part of an ASTM round robin where we have to separate out the instrumental characteristics of the accuracy of our measurement versus the experimental errors of the technique that we are calibrating to. There are five sites participating in this round robin. We have just finished the composite data, but we haven't done any statistical analysis. Probably in about 2 months time, Fiberite will have the complete analysis on the composite material.

Here you have, SC is the slowness (inverse of velocity) of the material. It is called URA #1 because that is the first parameter we print out on the software. The

calculated acrylic volume fraction and you see all the five sites, all the data falling into a very nice linear line. The correlation coefficient on this is like .999. It is perfect data in absence of any corruption on the destructives and all the five sites have different instruments. The five sites are Boeing Aerospace, TRW, Fiberite, Hexcel, and NIST (which is formerly NBS). The five instruments are very equivalent. It shows how well and how accurate we can measure velocity.

Bhe Are you working with a homogeneous sheet?

Ma It is. It is not an anisotropic material. In terms, I am going to show you some of the data on composites that is not part of the round robin material but this is one of the Hexcel data base which with composites, you see quite a lot of scatter. The instrument actually gives you several measurements to look at. You look at thickness as a function of % resin by volume and you see a very high correlation coefficient here using a thickness. The next slide we will show you is the ultrasonic parameter which is the time of flight as a function of resin content, also a very high correlation although here you do get a lot more scatter than the synthetic material. This is probably due to fiber area weight fluctuations as well as density fluctuations and other material property fluctuations. Slowness is the velocity measurement and this actually shows a larger scatter because you are dividing time of flight by thicknesses. We measure these dimensions very accurately. Thickness we measure down to about $\frac{1}{2}$ micron and time of flight, we resolve 1-2 nanoseconds so when you are dividing small numbers, you actually accentuate any extent of differences in material properties occur in these samples, it is going to show up in your ultrasonic data. The slowness inevitably, always has a much larger scatter than your time of flight and thickness data. I will show you some good velocity data, if you are very lucky, if your fibers are perfectly wet out, the ultrasonic is extremely sensitive to fiber wet out and a lot of this is due to localized variations of these material properties. If your material is perfectly wet out, this could be as good as .99 or .98 and the next set of data is from Fiberite and you see here the slowness data showing a .99 correlation coefficient. This is solution impregnation and perfectly wet out so you have a very good correlation. The next two shows you the individual parameters. This is the ultrasonic data, time of flight data, .999 correlation coefficient, and very small least square errors. The next one is the thickness data. Again, a .999 correlation with hardly any scatter in the data. I don't want to bore you with each individual calibration, but just to show you the data base that has been established. This is the Fiberite data base summarized. We have done some of the very high modulus materials and also some of their commercial materials, glass Kevlar, in combination with most of the commonly used resin systems, epoxies, polyesters, phenolics. We have done BMI's and here are the different correlation coefficients on the three parameters, thickness, time of flight and slowness. As we learned, or as we gain our data base, we have determined, or we have discovered that slowness

is a less reliable measurement of the volume fractions basically due to material property variations, like fiber wet out and density fluctuation, such that a lot of times, you know that your correlation coefficient drops quite a bit and in some instances, the slope of the curve is rather shallow so the Expert System software of the instrument actually screens for the best parameters to use to derive unknowns. Even if slowness has a high correlation coefficient and you still need a certain slope in order to get certain accuracies. It screens for that, and if it cannot use the slowness data, it will go to look at these two parameters and sometimes in some cases you will have a much less correlation coefficient from the time of flight due to material property variation and that wouldn't be used. There is a lot of built in algorithm to make sure you pick the most accurate correlation coefficient.

Thomas What is the difference between time of flight versus slowness?

Ma Slowness is the inverse of velocity so you divide your time of flight by your thickness so it is normalized for the thickness.

Thomas Time of flight is movement of the material under the NDE instrument?

Ma Yes, time of flight is the first time the signal arrives from this end down to this end. It is a through transmission technique.

Thomas Time of flight is a through transmission and slowness is movement...

Ma The slowness is actually the velocity of ultrasonic wave through that material because the thicker the sample the longer the time it takes, so you want to normalize it, so that it is independent of thickness. The slowness is ideally the best parameter to use if it wasn't so sensitive to material property variations, because it is normalized for thickness. You don't have to worry about thickness. Whereas if you use any of these parameters, it is dependent on thickness and you have to normalize it to a thickness per ply situation.

We have done, also, some parallel testing. We have established quite a large data base using the correlation relationship and we have some excellent correlation. Now the second question is, if you use this set of relationships to predict your unknown values, how accurate and how closely do you track the actual number. Unfortunately we have to compare to a destructive technique so we are bound by the destructive errors even though we could measure very accurately and I can show you some of the data that shows the intrinsic instrumental characteristics, you are going to see when we compare to the destructives, you are going to be bound by the variance of the destructive technique.

Here are results of the experiment we did. I might mention that the calibration data base was generated at Tempe at the R&D facilities and the parallel testing experiment was done in Orange. Two different instruments. The data base was transferred to this instrument and these are done at different times. The calibration was done a year ago and these were done, each one of these is a different production batch of materials and the dates they were taken and what we did was take samples out of the production and derive unknowns on the URA and then subsequently destroy the same samples and then look at the agreement between the two numbers. Here are the statistics of those numbers. This is the sample size. These are large samples that we took. The standard deviation and the variance of the difference between the ultrasonic derived number and the destructive number. You see these are very small. The standard deviation is always within $\frac{1}{2}\%$. Sometimes they are .81% with the Kevlar and I think that is probably due to some of the problems associated with destructive measurements of resin content on Kevlar. So this substantiates that the data base is quite stable and it is very transferrable and it tracks the destructives very well. The same set of experiments has been done at Hexcel. This is the data base at Hexcel. They have equivalent of about 20 something materials characterized and the material data base is actually growing. This is the respective correlation coefficient. A lot of .999, especially when you look at thickness and time of flight. Slowness, again, is a little more scattered. The next slide will show the parallel testing data in Hexcel. Each one of these is two batches, but Hexcel didn't supply me with the actual batch numbers and the date. You can see again, the parallel testing, the standard deviation here is well within $\pm \frac{1}{2}\%$.

Now I want to show you some of the intrinsic instrumental characteristics. This is a very difficult slide to read but I just want to show you this is 50 measurements using our instrument on a standard ultrasonic reference block made to ASTM standards. You can measure it 50 times and look at the variations of the measurement. We measured down to fractions of microns and nanoseconds, down here you see the time of flight measurements. This is in microns, so it is about $\frac{1}{2}$ micron in the variations. This is time of flight data, sorry. This is in nanoseconds. This first column is time of flight in nanoseconds and this is about $\frac{1}{2}$ nanosecond. The standard deviation of those measurements. The thickness, this is in I believe, centimeters. So you are about out to $\frac{1}{4}$ micron here, so the repeatability of this instrument and the precision is extremely good and if we translate this and I double the standard deviation, instead of $\frac{1}{4}$ micron in terms of mechanical measurements on the thickness, I doubled it to $\frac{1}{2}$ micron in the repeatability measurements or give it a little more room. Time of flight, I double it to 1 nanosecond. What we did was translated it out to on two sets of calibration curves. Obviously, these sort of errors, measurement errors, depending on the sample thickness and depending on how steep that calibration curve is, is going to have different effects. On a very thick sample, meaning anything above 50 mils to 100 mils. These are prepreg materials, and a

very steep calibration slope, the errors are within the three decimal point based on the instrumental characteristics. If you have a very thin sample and a very shallow slope, it is about .1%, which is a lot better from basically what we are doing with the destructives. This is basically what our instrument does, the current destructive techniques, you have a wide variance, at best $\pm 1/2\%$ if not 1 to 2%. We are calibrating to a destructive technique, but if you use a large statistical sample to calibrate, the mean of that population is going to be much more accurate and what we are doing is statistically minimizing random errors and, we could be more accurate because we are calibrating to a large statistical number and what we are doing is replacing with the precision of the instrument, the scatter of the destructives so that we could be more precise and more accurate than the destructive measurement. Once you are calibrated, your measurements are much tighter.

We believe that with this method and this is how I want to tie it in. How does this tie into TQM, total quality management concepts. Most of our traditional approach to quality is that we have a specification and we have a lower and upper limit of that specification. It is accept, or reject. Basically that is how we operate. Now the next slide will show that the true impact of product variability is not a step function. It is a continuous function. It could be due to various loss function which could be associated with basically the dimension, surface finish, various parameters and the sources of loss could be in scraps, all of that. Performance characteristics is really continuous, you are not cutting it off right here. It is a continuum. The performance characteristic as you deviate further and further away from the target value is not going to be optimum. What we are, currently our practice is not satisfactory, what you need is measurement techniques that will allow you to measure much more accurately. Right now your specifications $\pm 2-3\%$ and probably at best your destructive techniques are within $\pm 1-2\%$. You are really already covering this range. What you really want to do is to reduce your product variability around or within the specification. In order to do that, you need much more accurate measurement techniques that allow you to really truly measure the parameters, so you could monitor the process to give you this sort of situation where you could actually reduce the variability around the target value. It is a modern concept in design and manufacturing that we are beginning to be very much aware of, and that is where we want to be-constantly leading to more consistency, more uniform products, and more defect free products.

With that I want to summarize by saying that the advantages of the URA are that it is non-destructive. You could test it on the real material. It is faster. You see it in the video, it takes 1-2 minutes to take a measurement and give the result once the instrument is calibrated. It is a lot cheaper because of the labor costs and the down time, and the scrap rate and the rework that is associated with it. It is a lot more precise and more repeatable because of instrumental characteristics. It is a lot more

accurate due to statistical techniques that are employed in the instrument. It is a lot safer and cleaner because you don't have to deal with acids and the pollution aspects and the solvent issues. That summarizes what the technology is about. I will be passing out a reprint of a paper that is published in collaboration with Fiberite at the ASNT conference in October in Seattle. If you need further literature, if you want to give me a card, I could keep it on our data base and send you future updates.

Bhe What is in the MXB 9000 and is it epoxy?

Ma I believe it is. Maybe one of the Fiberite people have, is it toughened epoxy, or not?

Bhe Because, I guess, for the Fiberite all this list only has two phenolics, the rest are either epoxy or polyester.

Ma We haven't done much phenolics.

Bhe You only have one phenolic.

Ma It just demonstrates that phenolics as a whole, we could do it. I have done phenolic laminates as well for Morton-Thiokol. The principle is that the difference between the resin and fibers are significantly different in ultrasonic propagation characteristics.

Bhe One of the things, the dielectric monitoring of cures used successfully for the epoxy for the aircraft industry, but no work on phenolics. I think it would be interesting to see more data on the phenolics.

Ma Sure. We would like to establish the data on phenolics and I think Fiberite has plans to do some filled systems as well. We haven't done any carbon filled systems yet, but obviously we need some more data, but we need to work with the industry to establish the data. We can't generate the data by ourselves.

Bhe Also on the filled systems, when you look at it the filler is not randomly distributed.

Ma Yes, that is true. Localized variation of filler contents may present a problem, but if we are as sensitive to those kinds of variations then we may be able to use this technique in the initial phase when you are mixing the filler with the resin to make sure that that is uniform.

Armour What is the diameter of the transducer?

Ma About 1 inch. But you could choose any size you want. We have had as small as 1/4 inch and the largest is about 1 1/4 inches.

Thomas Does the diameter change the accuracy?

Ma It should not if you calibrate and derive unknowns with the same size. If you are more interested in localized characteristics, then you would choose a smaller transducer. If you are interested in averaging out, typically 1/2 inch to 1 inch is a very good size to use. We are currently, actually, implementing some enhancements to this technology. The current instrument measures fiber volume, resin content, and thickness per ply. We are currently implementing a heated transducer or we have a feature that allows you to acquire this data at elevated temperatures, up to about 400° and we are developing some data base from McDonald-Douglas in their processing of materials to develop a data base for them to interpret what is going on in the autoclave. With the heated feature, it actually would allow us to monitor and look at flow as well, as well as ablative prepreg which we cannot consolidate before. We are very anxious to proceed, the prototype was just finished a few weeks ago, so we are anxious to develop some new data. With that, if there are no more questions, I could show the tape first and then maybe you will have some more questions.

Pinoli Before you present that, Ed has some comments from the Fiberite vantage point.

Ma Sure.

Hemmelman I hate to admit this but Gloria knows more about what is going on at my company than I do. All of this work is being done at our Tempe research facility directed toward an unfilled epoxy matrix, Kevlar, glass, graphite, prepregs. Evaluation began in early 1987. We purchased our first URA 2000 in June of 1988, delivery in November, 1988. We have purchased a second one which is installed at one of our manufacturing plants at Orange, California. The ASTM round robin has been completed between the companies that Gloria referred to. They are doing parallel testing now with a number of production glass and Kevlar. What we intend on doing, we are getting some vibrations that perhaps this technique may not be applicable to filled matrix systems. We are going to initiate the program with our Tempe facility. We hope to complete it before the end of the year to get initial data. We are in the process of generating samples that have various level of filler, phenolic resin and filler on carbon fabrics. We will send those samples down to our facility at Tempe and get the initial evaluation run. We are also interested in the technique, if for example, it is not working with the uncured properties, perhaps looking at it for cured resin content. Most material specifications require documentation of tests for cured resin content on carbon-phenolic systems and as we all know that means

a high technology. We are also looking at it along those lines. If it doesn't work for prepreg, perhaps it may work with the cured...

Williamson If it just did that alone, it would be worth it.

Hemmelman Exactly.

Ma We will work hard.

Hemmelman By the next meeting date, we will have completed our initial evaluations and we will have some data to present.

Ismail It seems to me that you are trying to use statistics to calibrate a very clean system that you are using which is non-destructive against a very dirty system which is destructive. I don't know how good your statistics are when you try to do that because instead of having this wide distribution curve that transformed experimentalist, your statistics are converting it to a real narrow sharp peak, which is good in a way, but I am not sure how good this is in terms of applicability because if this guy is firing a nozzle, he is doing it the dirty way and therefore he is in that range where, in other words, your experiment might tell him he's okay here, but he fires it and he is in that dirty range where it fails. How good is your extremely clean statistical analysis compared to the real life.

Ma We haven't done those actually to answer you properly. I don't have any data to show you. You are right, we may be so sensitive using that line that any material variation that would put you out of range, using our technique or it may not truly, you know we are so sensitive to material variations. We don't have enough data yet. What I would like to see ultimately is to see that when we compare the two populations, the ultrasonic derived number is much tighter in measurement and the destructives will be much wider. We don't have enough data. We have instances where our range is just as wide as the destructives and in some instances we were narrower, 50% of the time. If we could clean up the destructives, it would make our life a lot easier.

Pinoli The thing I like about this technique is it is non-destructive, real-time and you can take action fast enough to prevent a lot of bad material being produced. This is real-time data that we could track and record. We sure need that.

Kraus Gloria, you might make some comments on what we are doing in signal analysis that might address that issue.

Ma This is just the beginning. We are a young company. We are only 5 years old and this is our first product and we are looking at a lot more sophisticated signal analysis to actually look at material property variations because when you see a lot of scatter in the destructive, you don't know whether it is due to material property variations or it's actually destructive experimental error. If we could have additional, the information we use right now is a very small part of the ultrasonic signal. We use less than 5% of the ultrasonic signal to get what we want right now and there is a wealth of information that could tell us porosity and other characteristics, fiber wet out, and we hope to be able to give enhancements to this so you could separate out what is due to material variation and what is not. In addition to giving you just a number of how much resin there, I would like to be able tell you how much wet out that fiber and resin intermix is and things like that. We are even looking at degree of enhancement, but we need to work with the industry people because I can't generate the specimens. I can generate the techniques, but I need the materials to develop the data base on and actually work on it. Some of the people here, I heard, were doing some aging studies. We would love to have some of those samples so that we could establish an ultrasonic characterization of these and looking at various correlations with the materials.

Buechler So far this has only been applied to flat panel layers, correct? Does any of the round robin members, have they looked at angle ply?

Ma No. Basically the current instrument is a laboratory instrument so we are only handling flat panels. We could adapt some curved, measurements on curved surfaces. Angle ply, no, that could be done. It is a matter of someone generating that data.

Buechler But you haven't actually looked at, cut a flat panel and attempted to look at it.

Ma No, not yet.

Bhe I think it would be good to get the effect of resin advancement.

Ma Yes. I would also like to look at some of the resins and filler without fibers because if we are sensitive to just resin-fiber mixtures, you know, we might be able to help in maintaining uniformity of that material.

I will show the videotape now. I apologize for the beginning two minutes of the tape because it may look a little more commercial than I would like it for this audience. Just bear with it.

Drake What is the price of this instrumentation?

Ma It is \$100,000 for the hardware and then there is a software usage fee of \$1 a sample. Instead of charging you up front a license fee for the software, we would just do it as a value to the customer. We price it very comparable to consumables of destructive techniques.

Drake In other words, you count the number of times the machine has been used and get \$1 for each time.

Ma The calibration curve, every time it is called up, is logged, but if it is establishing a calibration curve, there is no charge. There is no charge for developing the data base, but just using it.

Drake Is the machine portable or stationary?

Ma It weighs about 400 pounds and it is very sensitive. You don't want any vibrations. So it is not very portable.

Bhe Has Hexcel bought one?

Ma Yes, Hexcel has one. Fiberite has two. TRW has one. Boeing has one, but Boeing has one on a lease program.

Bhe I would like to hear from Don Beckley what he thinks of it.

Beckley Well, unfortunately, I started too soon. Gloria and I worked for about a year and a half trying to take the material of interest and we really struck out getting the acceptable measurement and the problems are as she has indicated. You have got to debulk a dry prepreg, get the air out of it, because the air is another component in that velocity measurement. You heard about cross flow, you heard basically that the third mechanism is the fiber being distorted as part of it. For all of us in our end of the business, with the little concern about filler thrown in. There were just so many pieces of learning curve. They were attempting to develop the hot press, hot stage to accomplish this. What I did was to bring pre-debulk specimens to the machine and we unfortunately didn't get results that worked. We are willing to try it again in the near term.

Ma We had just the heated element just about a couple weeks ago. We are very busy trying to develop a data base and getting the standardization activities. We are currently working the ASTM Mil Handbook 17 so that we get industry-wide acceptance on this technology. We have been very busy with Fiberite and Hexcel to develop the data base we have so far. Since we are very small and limited in resources, we put the heated transducer on the back burner. It is only in the last

couple of weeks that we were able to establish that, but I was just talking to Don at lunch and told him that we are ready for his samples now.

Bhe I think when you look at the phenolics, the typical material that we use in the ablative, it will be....

Ma Yes, we are definitely, we are ready to characterize some of those materials and I think that, I've talked with Don and he's going to get samples and Fiberite will have some samples. Hopefully, within a few months, maybe we will have some data.

Ismail How high is the pressure that you put on the sample and sensitive is the technique to room temperature fluctuations?

Ma The pressure, we could vary the pressure from 0-300 pounds and depending on the size of the transducer, it would range up to, if you use 1/2 inch, you could go up to 600 psi. The accuracy of control is within 1/4 ounce, so you can maintain very accurate pressure. It is all computer controlled and it is constant pressure. Room temperature fluctuations, I don't know whether we have some data on that, we could. the instrument is extremely precise and the alignment is very good. You could measure the deflection as a function of temperature. I don't have that data with me, but if you are interested, I can certainly get that.

Ismail I was just asking the question.

Ma We have done some of it and the difference is like 1-2 nanoseconds in time of flight measurements. Over the regular range of room temperature, it would get up to maybe 90° or 100°. This is usually in a controlled environment, air conditioned labs. That is not a problem, but you could also provide, there is a thermocouple, especially on the heated transducer, that would correct for temperature. So far, the effects that we have observed is within that noise level. If you look at the data, 1-2 microns and 1-2 nanoseconds is within the .1% resin content range.

Buechler Which group at Boeing has the equipment?

Ma Aerospace. Thank you for your time and all the questions.

Pinoli There is one subject that I want to move out of context, rather than moving on to carbon assay, in order to make sure we get this in. We have a contingency here from the Air Force and Aerospace Company that is in a position to give us more insight into the NASA-Air Force alternate source rayon program. I would like to move on to this subject and allow Major Opel to review the program. I think Ed has some words to say later as a follow up with regards to the Titan program.

Opel

What I have here is what we presented to JANNAF. I know a lot of you were there and Pat Fillingim did this in my absence. This is a quick overview of what we in the Air Force and at NASA are trying to put together to look at 1650 denier and 1100 denier and possibly qualifying a second source for 1650 but not for 1100 denier which is contrary to what some people want.

I just want to go through what our concept is, why we are doing it and then the flow of activities. We did have an industry review back in August at Aerospace Corporation. We did take the comments received from industry and integrate them into the plan. I want to go through the revised concept. That is, how we are planning to do this, the criteria for second source selection (I know that these are not final and all inclusive, but these are our first cut), and when we are going to try to make the decision about a second source and the timeline following.

We did a briefing to industry on the 16th and that was to inform industry of what we are doing. We were trying to get the input from industry and to get what kind of data base would be acceptable to industry. We were looking for comments both on utility and validity of the program, that is, can a program use the data if we come up with a generic data base for design studies. Is it useful? And is it valid? Will anyone use it? Also, we went over the test matrix content which is basically North American Rayon certification test matrix with some exceptions and some changes. CSD is going through a qualification for Titan 4 SRM and we want to make sure they can integrate what the government is doing and what industry is doing so we don't duplicate activity. We are trying to mesh the activities together so that we have one price to pay. We also had a presentation by the Astronautics Lab and by NASA on different test facilities, full scale test facilities and how we can do tests in government labs.

How did we get in this? I think everyone here knows that we have been in the rayon business for 40 years, since 1940, I guess it is 50 years now. We have never done a data base and so, and as the PAN effort is really starting to pick up steam, what we thought we would do is generate a plan of attack for rayon. Look at it and create a data base for rayon and use that as a stepping stone for PAN, saying we did this for rayon, maybe we can do it for PAN. Did it make sense when we did it for rayon, or did we find something wrong in the creation of this data base? That is one of the concepts we are trying to do. As you go through this, there are a lot of single sources of rayon all the way through. Every ten years or so, we have to change sources and it causes us to go through full characterizations and it's a three year down time.

I think everyone has seen this chart. This is just what rayon is used in and we talked about the two different types of deniers, going to three different weave

characteristics, going to all these different users and all these different combination of materials. You can see the 4926 listed in two places because of intermediate fired carbonization by Amoco, the VCK and also the VCL or CSA variation.

Who does it affect? It affects both government and commercial organizations strategic systems, tactical systems, space systems and everyone. It affects NASA, the commercial world, especially if you go into commercial launch vehicles and satellites. What kind of industries does this really effect? Everybody thinks, well rayon is just a simple material. These are the prime contractors on the left hand side and the first-tier contractors on the right hand side. When you start going down here to the materials levels, it doesn't affect very many people down there. It is the end product that affects everybody.

We also looked at rayon usage. That is how much do we actually use in the U.S. government in a year. If you look at that number, the maximum totals (the maximum number of launch vehicles, the maximum number of standard missiles every year) we would use about 2½ million pounds a year of 1650 denier and about 275,000 pounds of 1100 denier in the U.S. alone.

One of the issues was vulnerability, that is it is a single source, still yet to be fully characterized or qualified. We have Avtex material still out there, but it all belongs to program offices. There is no government stockpile of Avtex material. I just want to reiterate that because we always get letters saying we want x amount of your stockpile. There is no stockpile. PAN materials are not ready to go into production systems today and they may not be ready next year. It may be a couple of years away. There is not alternative there. If we had a surge and had to create more Titan 4's to do this or do that, as we go to peace time we might want to start taking that one off, but and the other thing was talked about this morning, uncertainty of regulatory requirements. EPA and OSHA, these two organizations are some of my favorite organizations. They have already driven three or four companies and different types of materials producers out of the country to Mexico, to produce some products, just because of EPA and OSHA standards. They are protecting American lives but losing American business.

Cost factors-If we go back to 1971, rayon was 78¢ a pound. The 1990 figure is NARC with the surcharge, \$5.65.? I don't know what it is next year without surcharge. Well, we have always been in a sole source environment and as you can see the price creeps up especially in 1988 when we had Avtex and then we went to post shut down and it went up almost three dollars a pound. If you are in a program, \$3 doesn't sound like a whole lot, but if you look at it from a total government aspect, if you take a \$1 increase in pound, that is a \$2½ million hit to

the government every year for that \$1. So a \$1 increase per pound for the basic raw material is a \$2½ million hit to the government, minimum.

The proposed effort was is looking at how we qualified systems which is through a full scale test, etc. What makes sense early on. We are talking about material characterization, that is characterizing what the fiber is and what the woven cloth is and what the carbonized product is, and what the impregnated material is and finally looking at some cured flat plates for mechanical properties, trying to create that data base. From there doing some small scale firings, really doing a 40 pound charge motor firing, so you have a data base of some sort and erosion characteristics. Very small scale, but it still shows you a trend.

After that you have to go into program specifics, that is building components, flight components, testing and qualifying flight components, doing scale testing, maybe doing scale testing instead of full scale testing. Leaving the option of doing scale testing or a motor firing instead of building a full SRM, or the potential to say that I have enough confidence in the scale firing that I will be successful with the full scale. This is looking at business a new way rather than saying we have to go fire 3 motors no matter what.

The first thing we are going to look at is the 1650 denier, low fired, 8 harness satin weave. We are going to do the characterization matrix, with three materials, Avtex and NARC which is already under contract through NASA, through MSFC, and an alternate source so that we have a data base that has 3 products, side-by-side so that you can see the family of properties that are acceptable for each product and the final results. 1100 denier-we are only going to qualify NARC. We are not going to look for a second source. There is no reason to. We don't use enough.

We are going to do the material property tests and I have some charts on what some of the agencies are going to look at. Starting at the basic fiber, woven fabric, etc., and do subscale static firing test and then let the rest go for program specific tests for qualification for their specific components.

The intermediate fired material, there is adequate supply to meet current requirements.

Mills

That is your assessment.

Opel

That is what the Titan 4 program office told me. That is what the Peacekeeper office told me, and it is what the small missile told me.

Pinoli What is the fabric product you are going to qualify in this program?

Opel We are going to characterize 1650 denier, low-fired, 8-harness material.

Pinoli What I am trying to clear up here is that ASRM is going to go to a higher firing temperature. That is a different product than what is being employed on RSRM or most AF programs.

Armour I thought they were developing a rayon source, not a carbon fabric source.

Pinoli They have to produce some carbon fabric to do the evaluation.

Armour That is okay, but you could always take the rayon and do what ever you want with it.

Opel I will show you step by step as it goes through. If you characterize the rayon and you characterize the weave, then you change the carbonization, that is where you have to restart the process. You don't have to restart the process at the basic rayon, because the basic rayon stays the same. It is just where you enter the basic sequence of events. We had the industry review on 16th of August. We had 25 organizations in attendance ranging from the rayon fiber sources to composite users to the government sponsoring offices. Sixteen organizations out of the twenty-five responded with input and opinions and requests.

These are some of the actions we took due to those. We are looking at moisture diffusion and microstructure of the composite, certify and define resins and fillers (I think that has to do with the numbering scheme or what is actually in that composite, so that when you go into the test matrix at Southern, you can pull out and compare apples to apples), timely dissemination of data (we are going to have meetings every 6 months to tell you where we are in our program and keep everyone updated, and as we get closer to the end of the program, who needs the data and where do you want it sent), and simulate hardware processing during flat panel fabrication.

There is a tape wrap demo. This is the composite materials part characterization plan. This is again the material characterization for the composite, cured composite. There is all the temperature range up to 4500, number of specimens. This is currently under review by Southern Research and Thiokol and Hercules. I think it is finalized now. We are waiting for a response from John Koenig from Southern to get the final numbers, but it should stay pretty similar to this.

What the revised concept is, and it really isn't a revised concept, it's just looking at how we can do this in a smart way. For 1650 denier, 2nd source characterization,

we are really going to do two buys. The first buy is going to be purchasing 50 pounds of carbon cloth fabricated to the NASA shuttle specification, delivered no later than 30 days after contract award. Let me tell you what is meant by this—I am not in a program to go find a new rayon source. I am in a program to characterize a carbonizable rayon and I want it demonstrated. I am not in the process to go out and start up a new source of carbonizable rayon. I want something that is already being produced, on line that I can characterize. The only way they can do that, demonstrate that to me, is within thirty days after I tell you that you've got the go ahead to deliver carbon cloth. I have talked to the people, and they do have carbon cloth available. There is no big driver there with that as a rationale. Prove to me that you can make carbon cloth out of it before I go buy it.

Pinoli What you are saying is, you're not going to deal directly with the rayon manufacturer, you are going to deal directly with the carbonizer. You are going to place your contracts at the carbonizing level.

Opel Southern is going to do that. The next thing is the purchase of material required for all the testing, specifications, and process documentation for operations up to producibility, composite lay-up and thermal/mechanical testing. That is, I want to go buy the baselined rayon and all the material I need and also I am going to buy the procedures utilized, documented procedures and processes, that we can use later for a base line for the product itself. The last part of this is the testing, because what I am going to do....

Pinoli Do you care if it meets the current rayon spec, since you are buying carbon cloth.

Opel Right.

DiMeo Is this North American or the second source you are talking about?

Opel The proposed second source. North American is the primary source,

Mills The source that you are qualifying for the 1650 is to be determined.

Opel Right.

Mills Not NARC.

Opel Right. For 1650, here is how the flow goes. We get the carbon cloth thirty days after contract award in an agreeable quantity. We will then ship it to MSFC where they will do some testing to look at prepreg, to look at whether it meets the carbon cloth specifications. Can they produce small sample, looking at resin contents and

do a little bit of testing there. After they do that testing to make sure it is a good product, then we are going to buy the thermal/mechanical testing because that is the expensive part of the program. I'll hold my decision on testing until I verify that the carbon cloth does meet specification, it is a good product. As you see down here the material, the basic rayon goes to Fiberite and Hitco and then to Polycarbon, US Poly.

Drake It should be Polycarbon and Hitco.

Hemmelman The carbonizers are Polycarbon and Hitco.

Opel Okay. I made a mistake. That is basically what we are going to do there. We are going to purchase A and B, that is the material to do the characterization of the carbon cloth to make sure it is an acceptable product and it is a good carbonizable product before we go buy the testing.

The 1100--primary source characterization is what we are calling it. That is all it is. We are going to purchase the total amount of material required from NARC and associated testing through SORI via task order contract at BMO. There is no second source for 1100 denier at this time. The rayon is shipped to Highland for weaving, shipped to Amoco for processing, shipped to US Poly. This is the flow for 1100.

Let me go through this time line real quick. Writing a task order and getting it through to Southern takes me about 2 weeks. I think we can start it in January, carbon cloth will be due February, interim industry briefing in May 1991, August of 91 all prepregged materials will be at either Southern or Thiokol, December 91 will be an industry briefing again and again in May of 92. Prediction is that testing will be completed and data base available for industry use in August of 92. Some people have pipe dreams or whatever, but I think we can do it in 20 months. We will see. It is tentative until the schedule can be worked out with Southern Research and based upon funding availability.

Criteria for second source selection--number one is that it must be a domestic source. The realization is that there is no domestic source, but law dictates that I have to look at a domestic source first. Demonstrated carbonizable product, that means I am not going to buy a pig in a poke. It has to be demonstrated. I am not going to go through 23 combinations of rayon. I want the formulation that they are going to use that they say is carbonizable and they are going to document that process and procedure. Market accessibility, that is, anybody can buy from them. It is an open market. The U.S. must not be the only customer of the product. I don't want a line that is dedicated just to sell to the United States. I want a line that we can tap into at any time, but we are not the sole supporter of that line. The government cannot

afford to keep two lines open all the time. There is another user outside the U.S. Cost will be a factor as will the long term viability of the production line. That is, I don't want to qualify a pilot line. I want to qualify a line that is there and will be there for the long term. That is kind of a judgement call. Some of the sources of data, NASA did request sources through Thiokol and there is still potential for presentations to the government, but that is still under consideration.

Pinoli On those judgement calls, if the manufacturer fails one test, does that mean he's is automatically eliminated or does he get a real low score and can recover somewhere else.

Opel He gets a low score.

Pinoli If he gets a low score on many aspects but comes up with a real low cost, will the cost factor override the other low scores?

Opel Yes, along as everything else is there, and scores well.

Pinoli i.e. Everything has a weighting factor.

Opel Yes, everything has a weighting factor. It is really judgmental, just like all source selections. There are other customers of carbonizable rayon outside the United States and I have been briefed on a couple of them.
Selection methodology, that is, how we do this. Ben Neighbors and I are going to sit down at the Officers' Club at Marshall and make the decision.

Opel Actually I did say that there would be members from NASA Space Division and BMO. I have tentatively set the 7th of December at MSFC. That may change to the sixth because of another meeting I have at Marshall. We will try and call all the people who are affected, especially North American, and also the people that we select and don't select on the 10th. Then we will put a notice out to industry by the 14th of December. That is our plan. There is more detail discussion on the test matrices that I don't have with me, but if there are any questions, I will try and answer them.

Pinoli I will throw the obvious question out. Has there been a change with regards to setting specification controls on the rayon itself? Originally we were going to, as I understood it, go along the lines of Avtex specs or North American specs and anybody who wants to qualify would have to meet the same specs.

Opel That was never the intent of this program.

Pinoli Okay. That clears it up.

Opel We have taken some lessons for the NARC experience trying to clone the Avtex material and finding it doesn't exactly match. What we are trying to find out is what is the key thing. And the key thing is carbon cloth. That is what gets you your performance so let's specify that and then let the people behind that, the rayon producers and weavers, tell us how they got that specification.

Pinoli Then obviously North American Rayon is in a position to work with the carbonizers and compete for that particular product too. Right now it is frozen on most programs to rayon specifications.

Opel What we are trying to say is, I don't think many people in here are smart enough to tell me what 18 properties on rayon we should specify and within $\pm 2\%$ on each one. I think we can come up with a list of 46 different properties maybe. There are probably 4 or 5 key ones that really need to be controlled and who better to tell us who can control those than North American, for example, or whoever the other source is, as long as the carbon cloth that comes up from the carbonizers meets the NASA specifications.

Pinoli The problem I perceive here is NASA for RSRM. Ben Neighbors, sitting on the RSRM program, which put rayon specification controls. I don't perceive that he can possibly introduce an alternate source material into his program without maintaining the same clone-type specification control that he has at NARC.

Opel That was one of the initial issues that we had to address, and they had just gone through the heartburn of trying to get North American to clone and go through 23 variations of rayon to get there. We decided to say where do we really know what material we want. That is the carbon cloth. Let the carbonizers and the weavers and the rayon makers tell us what process they used to get there instead of dictating the process.

Golde That is going to be cast in concrete after the carbonized product is nailed down.

Opel Process and procedures they used and what parameters they are going to control and to what level they are going to control the parameters are deliverables.

Golde I agree with Pat, though. Right now we have a spec for the NARC product and if we introduce this it might not look anything like that spec.

Opel Let me give you an example. I was in France in September to qualify a French company to build batteries for U.S. spacecraft. Over there I put three mandatory

inspection points in. The U.S. guy has 22 mandatory inspection points given him by NASA. Why half of those mandatory inspection points are required is because they have lost control of the process here, and they are trying to get it back and figure out what are the key parameters. They go look at one and all of a sudden it is not the right one, but if you spec it anyway and then you go look at another parameter and now I think they are up to 22 different mandatory inspection points. The French company that provisionally licensed the U.S. company has three. We may be in this situation with North American. I am not sure. What we are trying to do is say, industry, you tell us.

- Mills I think you might be advised to talk to the carbonizers rather than just your rayon source. You'll find that all of the specifications, at least the ones at CSD, invoke indirectly the Amoco specs.
- Opel When you cure the carbon cloth it will have the documentation of the entire process, rayon producer through the weaver through the carbonizer. If Amoco comes up with a specific process because they have to change a time or temperature, that will be in that process.
- Armour Point of interest is that ASRM program is developing or has a materials development program underway as we discussed earlier and we are not bound to use that spec that you are talking about. We are going to come up with our own material and our own specifications.
- Opel I guess most people do use that carbon cloth spec right now. If ASRM changes at least you will have the data base for rayon, for the weave, for the woven cloth. You will have all that specified and you will have a variety of choices from the data base to compare with to see if your properties are in family or out of family. Then you are going to change your carbonization process and then you are going to create a new data base. That is where I think this numbering sequence that you are talking about, the coding makes sense. When you want to tap into the data base at Southern, you call up, whether it is the carbonization spec or whatever, you call up that level and it will tell what data is in there and what material. The materials that we are talking about are the top one, plain weave, three ply. 1100 denier and the bottom one, the 8 harness satin weave, 1 ply 1650 denier. We are not going to do the five harness satin weave and it really leads you into the high temperature fired graphitization material from Amoco, WCA, which is really Poly 5014 and then the low temperature fired carbonization, we are going to do US Poly 5055 and Fiberite 4926.
- Drake If anybody else would like copies of this briefing, I will try to get them a copy.

Pinoli Your next, Ed. Ed Mills is going to give us an update on the 1100 denier qualification program that is underway at the present time for Titan. He will give us an overview and let us know where it is going.

Mills Basically Titan 4, the original Titan, anyway, has a requirement for North American based rayon prepreg in the form of WCA cloth for FM5014 and VCK cloth for MX4926. Our requirement is driven by a little bit tighter schedule than the schedule we saw a few minutes ago. We are proceeding, it was my understanding that this was funded, it may be funded at our risk, I am not sure, but we are proceeding full speed ahead on an accelerated schedule. This is just to give you a little bit of an idea of where we are in hopes that by our opening up, we can coordinate some of the efforts and streamline both programs, maybe, and at the same time encourage the Navy and some other people to reciprocate. The basic Titan design, this is about a 40-inch throat, uses flatwise involutes graphite phenolic here. It uses a parallel to centerline tape wrap graphite phenolic here and silica phenolic, which we are not really interested in at this point. There is basically an entrance ring which is the VCK, MX4926. This reiterates what I just stated. This should be perpendicular to contour.

The material is basically the same design that we qualified in 1964. Some iterations have been made on the design in terms of number of rings, increased performance, and number of segments and this and that. It is basically the same generic design that we have been flying for quite a while. We originally qualified that with the IRC rayon. In 1978 we changed to the Avtex and we did a series of qualification tests including TM3's and full scale static firings at that time.

Just to give you a quick pedigree and I will try to be reasonably brief, the 4926, our specification controls various things such as density and carbon properties of the cloth. There is an Amoco spec which in fact controls the rayon properties and what we use, I guess it is now grade 425. The NARC material will be 435. 425 is the same spec except Avtex. The 5014 is a slightly different generation specification, but it is still a prepreg and a separate spec for the WCA cloth that controls density and various parameters of the carbonized cloth. The rayon cloth is once again controlled by Amoco specification, which also goes down as far as the yarn level. Grade 430 is the NARC, 420 is the Avtex.

To give you an idea of the parameters that the Amoco specs control--as was mentioned the WCA is a 3 ply, plain weave. This weight and number of ends and number of picks per inch, tensile strength, s-twist as opposed to z, similarly for the VCK and the point I was trying to clarify a moment ago, the intermediate fired is at 1500°, the high fired is on the order of 2500°. As I understand it this is the one that the Air Force for 1100 will concentrate on.

Again this is the RM2284A which is identical in terms of requirements to the RM2284 from 1977 for the yarn which is z-twist and which is 1100 denier as opposed to 1650 for the shuttle type material. I don't think that there is a lot that is drastic. Twist is slightly different. The denier is obviously different, the conditioned elongation is slightly different. The strength is slightly different. All of these are basically parameters that relate to the denier. There is one item that is somewhat different and I traced this all the way back to 1977. This is a slightly higher number than what is allowed for the 1650. I don't believe this a concern. The next chart is one I stole from Pat which he gave us last year that shows the various characteristics. The high fired is basically the WCA, this is the VCK and this is your CCA-3, CSA and VCL type material. Probably the most interesting thing to me is moisture adsorption and ash content. There are some other things that are different, but basically I don't believe the ash content of .7% is a problem for us.

With respect to what we are doing for qualification, there is actually 6 parts to our matrix. It is a fairly extensive plan which I have recently provided to Major Opel and the Aerospace Corporation. The prepreg characterization, really there is an item out here that is not on this chart. We are very interested in the raw rayon properties, both yarn and cloth. I was talking to Ken last night and he expressed some concerns, so I'll tell you that we do plan on doing that in terms of looking at the data base and specifications. The data base will go back to some 1981 data that I have extracted for WCA based rayon material. The prepreg will include the manufacturer's testing for specifications, their specifications and again correlation to the data base from the Avtex material. There will be three lots and by lots I mean three different heat treat runs from each of the materials, the 4926, 5014. It will then be put into a subscale motor, TM3 and there will actually be three static tests with instrumented nozzles. We will be comparing 2 NARCs versus 1 Avtex for baseline and versus the history for 1977 and 78. We will also fabricate coprocessed panel of both Avtex and NARC material which will be used for SORI type testing. It is actually an abbreviated matrix, the same matrix that will be done here. We will fabricate full scale components, standard NDE and tag end acceptance test. Additionally we will fabricate a more extensive set of coprocessed panels for full characterization and we are also going to look at the tag ends themselves so we get the concern that was expressed earlier about using actual parts as opposed to just test panels.

This is the TM3 nozzle. It is about a 3½ inch diameter. The throat will flat wise involutes using graphite phenolic. The exit cone will be parallel to centerline graphite phenolic. This is essentially the entrance cap I was discussing before which is the 4926 VCK which has an orientation roughly normal to the flow.

Instrumentation, this is an established set of instrumentation. Maybe not as fancy as some of the more recent ones, but it does include thermocouples imbedded in the carbon-phenolic and the 2 graphite-phenolic throat rings and the exit cone.

We intend to do the thermal characterization at Acurex/Aerotherm. The reason being we get high temperature, high flux rate, charring input. That gives us both a direct comparison to our existing data bases and direct analysis input to the analysis codes. It is significantly more expensive than the SORI type testing which is more basic but does not give you the high flux rate and direct input. The mechanical characterization will be a full matrix which is similar to the NASA level 2 matrix. It is actually slightly abbreviated and tailored based upon what we feel our needs are for the graphite-phenolic and the intermediate fired carbon-phenolic that we use. The abbreviated matrices go up to 1200°F and will address multiple lots, multiple processes including press cured panels, low pressure autoclave on the order of 250 psi and high pressure hydroclave on the order of 1000 psi, with and without post cure and it will also address the full scale tag ends. Then we plan to do an analysis with the data we get. Depending upon what we get, there is also a contingency for a full scale test, however we do not believe that is necessary at this time.

This, I will just present and you can peruse it, I'll let you peruse these since I am not a thermal analyst. Pete Melra tells me that this is what we need and that it will provide direct input. The majority of these tests being done on both charred material, high flux rate and virgin material.

Bhe On your post cure, are those on laminate, or what kind of sample is that?

Mills The cure, post cure is full scale. Coprocessed panels that will be done with the full scale parts as well as the tag ends which will be from full scale parts.

The matrix that we have got is essentially similar to what Major Opel put up with the exception being our temperatures at TBD. We will base on the actual thermal expansion tests down here, the high rate expansions. We have four intermediate points where he has seven intermediate points and in the most case we have three specimens where he has five. You will find that there is no SORI type thermal testing here at this time because we are using the Acurex/Aerotherm. Also the heating rate is 30°F per second, I believe his is 50, but if I am not mistaken SORI feels more comfortable using the 30° unless they have improved their capability recently. That matrix you just saw went to 5000°. This is the abbreviated matrix for the coprocessed panels and I will show you in a moment the matrix of the materials and where they go into this. There is also a little mini matrix of moisture content and generic miscellaneous things that will not be repeated for all materials but will be done. The ply lift is probably the most interesting of those. This is

where we get our material. Prepreg manufacturer which will press cure panels with no post cure, three lots of NARC 5014, three lots of NARC 4926 VCK, coprocessed with the TM3 hardware which is going to be autoclave cured at a reasonably low pressure, 200-250 psi. We will have 5014 NARC without post cure and with basically our exit cone is not post cured and our throat rings are post cured, is the distinction there. We will have 4926 VCK and we will have Avtex baselines of each of those three. For the coprocessed full scale, we will take the 5014 which has an extensive set of non post cured panels and a lesser set of post cured panels. 4926 will have a full set and we will take the tag ends. We will also take same source of material for miscellaneous testing.

I hate schedules but this is essentially the schedule for the thermal properties which shows basically January 92. Prepreg manufacturer is basically up here, including panel fabrication which is completed even though it doesn't show to be completed until March of next year. We are somewhat accelerated time line and that is completed now. The TM3 nozzle is not yet very far along. The full scale, if I am not mistaken, the coprocessed panels are complete and about to shipped to SORI if they haven't already been shipped to SORI, since we are under pressure to accelerate our decision points. Right now we are showing authorization to proceed to build the first flight nozzle mid to late part of 1991 which is somewhat before the other date that Major Opel's effort would be available.

Just for the purpose of throwing out some information, this isn't guaranteed to be complete, but the users of the 1100 denier WCA graphite, as I said Titan has a program underway, Mk104 standard missile, I believe, has fired four motors. There are a number of other users than the 2D carbon-carbon. Hercules is leading with their third stage Peacekeeper. There are other programs, IUS and Intelsat will benefit from this work and presumably some of these others will benefit from our work.

My conclusions, basically we have a substantial amount of work that is underway. We will have the first twelve sets of SORI test panels roughly 6 months from now. That is raw data 6 months from now. The remainder of the test should be complete by the end of next year. With respect to the proposed Air Force matrix, we are generally consistent, although we have less tests, both in terms of columns and in terms of repetitions. We do not do the thermal properties that are in the Air Force matrix because we are relying upon the Aerotherm data. There will be some spare panel material and we discussed this last night. I didn't realize quite how much difference in terms of quantity of material that there was, but there will be some material available that we could entertain a cooperative effort and I would encourage it in terms of having SORI do a supplemental matrix to what we have to answer some of the Major's questions in an earlier time frame with less expense to the

government. There may be some additional unprocessed material in that the TM3 parts have not been started and it may be possible to get additional material dedicated to panels if necessary. My recommendation is that we coordinate our efforts and basically share the data. I would also recommend, and this may be somewhat controversial, especially here, that we consider second source. I believe based upon a previous view graph there are enough users out there across enough programs to justify it, even though we do not use the quantity that shuttle uses. That's it. Thank you. Questions?

Bhe So on this qualification, if every thing comes out no surprises....

Mills We don't expect any surprises.

Bhe Wait a minute. The mechanical properties, thermal properties within the family on side by side comparison, you mean a full scale firing?

Mills At this point we believe that we can qualify with TM3 firings and analysis based upon the SORI testing and the Accurex Aerotherm testing. If the data shows that we have big differences, which there is no reason to believe at this point in time, based on the work that has been done so far on the 1650, although I point out that this is higher fired material. You are talking about something that is fired around 1300 and I am talking about something that is fired at twice that, so although we believe we have no reason at this point in time to expect that there is a difference, we are doing the tests to assure ourselves and our customers that we have a legitimate product that will be a direct replacement, but at this point in time, we do not. There is a contingency that we do not plan to do a static firing.

Buechler Ed, what has been your experience in terms of thermal property data that has been obtained from SORI and Aerotherm? How do they compare?

Mills I don't know that answer. That is a very good question and that is one of the reasons I would like to see the supplementary matrix include testing at SORI on the same source of material, same pedigree, so you will have a direct correlation. In general we think SORI does very good work. I am not taking anything away from their capability, but we do prefer the high flux rate.

Buechler I was just wondering if you do have a comparative study...

Mills I do not. It may be that other people have that data base. I would suspect that the people who are relying exclusively on the SORI data have something like that. I don't, it may be that Pete Melra has it, bug me about it next week and I will see what I can find, but I don't know what that is.

Buechler The reason that the contingency is under the Titan program, didn't want to get to the point of finding out that were major differences and not have the capability of doing a full scale test. That is why the contingency aspect of doing a full scale firing was requested and has been imposed.

Mills And if we don't need it, the parts go the first flight. So we are ahead of the schedule in terms of first delivery.

Buechler Just consider it to be available if needed.

Pinoli I would like to ask one question of Myles while we are on this subject. Are you going to continue using the upper limit of .70 for ash content in rayon for your product or are you going to reduce it? How can you justify such a high limit?

Towne Nothing comes close and we are talking about the high fired material. I think we will probably be dropping that just to be consistent.

Pinoli I know Avtex set a lower limit in about 1985.

Towne It was just a hangover.

Pinoli It is just an old spec that hasn't been updated. I would not like to see rayon above 0.35 ash.

Towne It was a ridiculous requirement to start with.

Pinoli Bob, what is the current ash content in NARC rayon?

Looney I think it is between .25 and .30 on the average.

Pinoli I think we reduced ash to 0.55 for the Hitco spec. Don?

Beckley I remember .4, Pat .

Pinoli I know we had some trouble with real high sodium coming in from Avtex onetime and that is what drove us to reduce the upper limit.

Mills I will throw this out. I have got data from 1981 Avtex back when we were making "good" WCA that is .53.

Pinoli That was the stuff that was giving us some headaches on low fired fabric. That does come through to the end product low fired fabric. On high fired fabric, it all goes away anyway.

Mills I don't think you are going to see it on the NARC material. I agree with you, in fact, this "excellent" material that we had of the 1981-82 vintage, in terms of physical properties and performance, has been as high as .53.

Pinoli I am going to move on to one small subject and then we will adjourn. We will pick up the last two items over at North American tomorrow.

The subject that I wanted to talk about just briefly here is carbon assay testing, to bring people up to speed on carbon assay testing. We have had some concern for a while with regards to the test precision and test accuracy of data being generated by all the carbonizers. To give you some idea, Hitco uses a LECO carbon analyzer to run all of their products. Polycarbon also uses the LECO carbon analyzer and Myles Towne at Amoco uses a totally different system which is called the train setup, which you actually measure the CO and CO₂ by adsorption technique. It is the old method but it is a good method. It takes a lot longer to run a carbon assay by the Amoco technique but I place more confidence in the data. Mainly I don't know what goes on inside of a LECO analyzer. It is a black box, you put a piece of material into and out comes a number that is your carbon content. Unless you know what is going on within that black box, it is pretty difficult to say what the test accuracy is. In order to get a handle on it, we've taken some calibration material from one of the suppliers, in this case Polycarbon, and we are in the process of round robin testing that product. I'll show the raw data that has been generated for your own edification.

This is really fresh data, so forgive me for not summarizing the test results and coming to a conclusion. This has all been done in the last couple of days. The obvious thing is that we have a variance running as much as 2% with 95.3 at one laboratory and 97 at another laboratory and 96 at another. It would lead you to believe that on the same calibration material, we could see variations of up to 2% depending upon which laboratory ran the product. One of the reasons that this issue came up originally was on the RSRM program we are trying to get a handle on whether a product at 96% carbon assay was better than a product with 98% carbon assay. In reality, what this also reflects is we don't have test reproducibility. We don't have test precision sufficient to say within 2% as to what the actual number is on a RSRM type carbon fabric. This is just more heartburn from the standpoint of how to utilize the data that is out there. The data that is out there was based on testing by each one of these laboratories independently and within each one of the data bases at that laboratory, I suspect we have good data, but if you are trying to

compare data from different carbonizers, you might be in trouble. I think that is the message that is coming out. The corollary and follow up to this is, we need more work between these laboratories to find what is the basic problem. Why can't we duplicate results from laboratories. It is obviously not a materials problem from this standpoint. It is a testing problem. I think we should discuss the issue with LECO and find out why this kind of variation comes up. This will be a study program to be carried on.

Ismail

Which one is LECO?

Pinoli

This is LECO and this is LECO over here. These two are LECO. The higher number is showing up is here. That's Myles out at Amoco. Cindy would like to relate that she has had wonderful results with her LECO at Marshall.

Hall

We have just a little bit to finish up with our program from yesterday and then Bob has a program for us this morning so does anybody have any questions? Is there any leftover business from yesterday that we need to take care of before we get started this morning? If you need handouts, check with Sherre. Make sure that we are up to date on handouts.

Wayne Johnson from Highland is going to make a presentation and then we will go from there. Wayne.

Johnson

I was asked to make a few comments about rapier weaving. Basically Highland, then Burlington changed its weaving operation in the industrial business in approximately 1981 and removed all of the existing shuttle weaving machines and bought and had 2 types of looms. One was a projectile loom which is typically produced by the Sulzer Corporation. It takes the yarn and picks it up with a little bullet type device and shoots it across, carries it back under, and they have about 15 or 20 of them operating, like a machine gun. The other type was a rapier loom. If you have seen the Indians throw their shuttle across, that is essentially what a shuttle weaving machine does. You wind the yarn on a quill, a little spool. That goes into a shuttle which is about 10" long and goes back and forth across the loom and latches, or catches on either edge, which is called a selvage. It is always bound down. The determination was made that the rapier loom was better equipped to handle heavier yarns, particularly such as aerospace, Kevlar, and other heavier yarns that go into the industrial weaving business. In the process of that, sufficient shuttle looms were retained by Burlington to handle the rayon aerospace business. About 2 or 3 years after that, we started doing some experiments on rapier looms with the aerospace products. We made WCA, VCK, VCL, CCA-3, CSA all the numbers and designations, 8 harness satin, 5 harness, and plain. We did have some early issues of about how you tie the edge down. There were some problems as the sampling

developed with edge curl. There was some problem with distortion at times. The selvage area on a rapier loom is different from the shuttle loom in that fill yarn is fed from a package. You have a rapier arm which picks up the yarn off the package and is metered to the width you are trying to run. It carries it to the center of the fabric and then another rapier comes over, catches it and carries it across and it is cut on each end. What you have to do when it is cut on each end is find a way to bind these down and that is done by some different rayon yarn which is put together in a what is called a leno weave. It wraps around these filling threads and holds them in place. So, we did a lot of work with initially with Hitco, subsequently with Polycarbon and with Amoco, and gradually the processability of the fabric were pretty well-established. We had some serious questions about the rapier, because the cloth, as you know, by the time you process and carbonize it, shrinks roughly speaking 30% in both directions. That has pretty well been resolved. We have been running the same selvage construction now for about 3 years. There was some early work done about 4-5 years ago, perhaps, and part of that went into shuttle, part went into D5 and today we are producing fabric for NASA, for DOD, principally D5 and so far we have woven approximately 800,000 pounds of rayon on rapier weaving machines. When I say there was a problem with distortion earlier, I think that was more a phenomenon of the time than it was anything else, because about that time which is about 1984, there was a serious effort put forth by the carbonizing community to improve the alignment of their fabric. It really didn't make any difference what you were running, there had been a lot of distortion in fabric before and it is still a problem. The industry, particularly after STS8A, really cranked down on all your quality assurance people to not want to see anything that looked out of place in woven carbon or graphite material. At that time, recognizing the importance, we got on Avtex's case and said, look guys, you have to get the yarn more uniform. We got on our own people's backs and said we have to reduce the defects. We have to do a better job and so collectively, we materially improved the quality of the product. When we went to try to present rapier weaving in roughly 84, it was a nice conversation with everybody but Harry Marrug. I went in to see him one day about rapier weaving and he didn't get up and shake hands. He just said, you know the Navy never changes anything. In any event, no one wanted to go forth with the rapier weaving. It didn't really seem to be required at the time. The cost and qualification, everybody was nervous about any changes and so we sort of dropped the subject. Then when the issue of Avtex and NARC surfaced, the determination was made, well, if we are going to qualify NARC, let's do the whole thing.

I have two samples I am going to pass around. The one major change that we have made has been that when we started weaving this, as you will see, we had a longer tail or fringe on the edge. That presents some problems, particularly in prepregging, because that resin has a great affinity to want to latch right on here. That has been

shortened. I am going to send two samples, one is the older version and one is newer. I think you can quickly identify which is which.

We have, let's see, all of the 1100 denier, in fact everything really, that has come from North American has been woven on rapier looms except for a few very early samples in the evaluation program. One set was done and everything but the re-entry program for D5 has been woven on rapier. We have woven VCK rapier. We have woven a fairly substantial amount of WCA rapier. We have woven a lot of 8 harness satin. The reports from all the carbonizers which have been recently canvassed and confirmed, are that the rapier material is processing quite satisfactorily through the process of carbonizing and also through prepregging. We contended in the early onset of this that if you went to rapier woven fabric, you would reduce the cosmetic defects, I am going to call them. They typically didn't cause a lot of problems, but they didn't look pretty. We said we could reduce those roughly 50% by going from shuttle loom weaving to rapier loom weaving because that shuttle changes every 4 inches. In any mechanical device, anytime you have that going on and change the shuttle that often and all that stuff, it is the biggest single weaving problem. The rapier essentially, completely eliminates that. We are pretty happy with it. I think the fabric improvements in shuttle loom production, made since 1984, have been significant. The rapier material, still is a better, more defect-free product than the shuttle woven material, but it is not 50% better anymore. It is probably 25% better because the shuttle material has gotten better. That is about all I have. I have checked with Don Beckley, I've checked with Bob Beighley, and through the prepreggers as well. I did get some input, really from Fiberite, concerning this tail length and we understand that and that is why we made this change to reduce the tail length. That is all I have unless there are some questions.

Pinoli Just one question, Wayne. The leno on the selvage edge is obviously a very light denier. Does North American make that? What is the denier?

Johnson I think it is a 300 denier which is twisted and plied and we buy it from a third party who buys their raw material yarn from North American. It is a textile yarn. It has been used a long time. It is North American yarn and we buy it because it is tightly twisted in order to get the grip on the yarn and to run all its little doodads.

Pinoli How about sizing?

Johnson Sizing? We use no sizing.

Pinoli There is not sizing at all?

Johnson No.

Pinoli One reason I don't have much concern over that stitching is that the selvage edge is always turned off anyway. It isn't something that gets into your end product. Nobody has ever considered a separate qualification just for that.

Johnson Well, NASA wouldn't sign on it. They said they had to qualify it.

Buechler Do you also just accept this leno thread on certification or do you verify that there is no sizing?

Johnson I don't know the answer to that one. I don't know. I had heard about the silicone issue. I would be 99% sure that it doesn't have any silicone in it. We have seen no evidence of anything throughout all the time we have used it. I will check that for you.

Golde Wayne, I wanted to make one comment, too. It has nothing to do with selvage, but it concerns rapier fabric. We have been qualifying both, demonstrating both rapier and shuttle fabrics in our forty pound motors. Some of you may have heard a rumor that the rapier is falling in our 40 pound motors more than the shuttle material. If you look at the whole population, that is probably true. If you get down to discriminating between draper and rapier, there is really no consistency there at all. We have got two more 70 pound motors to fire and that's 2½ the burn time as the 40 pounders. So far those look real good on all the rapier material. We do not, right now, Thiokol does not have a problem with accepting the rapier fabric. We get small erosion pockets within the throat of the motor which is typical for a number of 40 pound motors. In case anybody hadn't heard that, we haven't really discussed it in our telecons with NASA because it is too, we haven't completed the whole 70 pound series.

Hall We also have a full scale firing coming up on December 12 and I think in that one we have rapier and we also have NARC and I think we will have some Avtex restart.

Golde No, it's all NARC.

Hall The loom?

Golde There is Milliken and Highland.

Hall This is a very important full scale firing coming up the 12th of December. We are qualifying three different things in one, or working on three different things in one firing. It's going to be a very interesting full scale firing coming up. Pat, do you have anything else?

Pinoli I don't think so.

Hall Does anybody have anything to do with the regular part of the meeting before we turn it over to Bob and we do the plant tour?

Johnson I would like to make a comment. I was asked a question and I am going to check more in to. it is our experience in running North American yarn, vis a vis, Avtex. My one liner on it, which I have directly from the plant, is that the North American yarn runs equally well as Avtex, if not better. I think I would say, from a processability standpoint and a uniformity standpoint, I think North American has done an outstanding job with what they have shipped to us. I just thought everybody would like to know that it is processing extremely well.

Hall We appreciate that and again, let me thank all of you for participating in this meeting.

Towne Are we passing up on the low-fired PAN activity? Are there no new firings?

Pinoli Yes, there has been sub-scale testing on low-conductivity PAN fiber but it has not been reduced in time for this meeting.

Bhe I have a question for Wayne Johnson. He said uniformity or something. Is that talking about the size?

Hall I think he was talking about distortion.

Bhe When you mentioned the uniformity, what is that?

Johnson One of the problems we used to have with Avtex yarn is they sort of drifted around on the yarn side and they also drifted around on the strength. Since we do statistical tracking behind every shipment we get before it is committed to weave, we keep all those records and anybody can see them. We found too often that we had to blow the whistle on Avtex and say, look fellows, your trend is drifting. If that trend gets started and you don't get it straightened out, you fall off the cliff and you are out of spec. My consistency comment simply says that finish, for example, that North American is putting on the yarn has been very uniform, very predictable. Their yarn size has been right there, the strength, all the properties have been quite consistent within the parameters of North American yarn.

Pinoli I think that something should be said for the fact that a lot of people don't realize that the weaver does a lot of cross checking on rayon properties. He doesn't totally rely on what the manufacturer tells him. Until recently, everybody just looked at

the carbon fabric and assumed that everything was being done properly back at the rayon level. Wayne has always tested the yarn to verify it and met specifications.

Hall Anybody else? I would like to express our thanks, the committee's thanks to North American Rayon for sponsoring this meeting. You have been very gracious hosts and we have all enjoyed it tremendously. We appreciate it.

Looney Thank you, Bill. It has been our pleasure, certainly. There are three people that I want to be sure that you meet. Ralph Markee came late last night by the restaurant. Well we all remember Ralph. We would like for you to meet Tony Butts, our vice president for personnel and a member of the board of directors of North American Rayon.

Butts I just want to say a word on behalf of Charles. I know that if he were here, he would echo this. We are very happy to have all of you here and hope your stay for the last couple of days has been enjoyable. Anything we can do today to make your stay enjoyable and educational, we will be glad to do that. Just call on any of the staff here. We just welcome you to East Tennessee.

Looney I would like for you to meet, also, our chief environmental honcho, Dr. Lou Rausch. Lou is going to be here while you are here to make himself available for answering any questions or concerns you might have in that regard. Thank you, Lou.

We have a short video that we want to show you that describes what we do for a living here. It will take about 8 or 9 minutes and then following that I have a brief presentation, using the viewgraphs. Then we will hit the road. We are going to do a very fast tour of the plant, starting with the first of the manufacturing sequence and following stepwise right on through. Then we're going to let you go to the chemical lab and the physical testing laboratory and view those and if you have any questions, you might have them answered on the spot. Otherwise we will come back up here and have them answered.

Let's spend just a few minutes going through a few things that are important to us and we want to share with you. The first, of course, we got this from Rick Golde. Rick, thanks for letting us use this. This is the statement from Thiokol that says up to the point of qualification, that they see no problem with the product and we are going ahead with the qualification phase. That is something that made us really happy.

Some points we want to make include trying to draw differences between us and Avtex because it is very important to us that we are not painted with the same brush

as Avtex because we feel that we have our act together and we are doing things as they should be done.

We understand why there would concern and we understand why there would be concerted effort to find a second source. At the same time we want to make some contrasts. Avtex was highly leveraged buyout. They had a lot of debt service. The bulk of their production was rayon staple which is a very low profit margin item. Staple is what you recognize as a bale of cotton. It looks like cotton. It is chopped up, and cut up, and then, it is blended with polyester or whatever and woven into clothes and what we make is continuous filament. We have niche market that is used in some very expensive and very attractive dresses

Avtex produced massive quantities of the product, 200,000,000 versus our 25-35,000,000 pounds. As a result, they had massive quantities of chemicals for disposition and in contrast we are a much smaller plant. Essentially they were controlled by one individual. Being a an employee-owned company, we have a stability of commitment that is perhaps in contrast to such an arrangement. Being employee-owned, the board of directors and the officers of this company have a different management style and a wholly different commitment.

We have kept pace with environmental concerns. We have made a lot of new additions to the company and modifications. We have added personnel. We have added facilities. We are still doing that. There is a list of things that are going on to be sure that we speak to those environmental concerns that will not get us into trouble. We have a clarifier being built right now that will increase out settling capacity by over 100%. We have a new sand filter. We have a new dewatering facility that will be in operation this spring. We are not standing pat. We are trying to keep ahead of the environmental concerns.

Unlike Avtex, we treat all of our viscose waste. We don't have basins of viscose liquids sitting out in the field. We also have recognition by the Trout Unlimited. We have plaques that were given to us by Trout Unlimited, praising us for the work that had been done to clean up the river and to be sure that it is kept clean. As a result of those efforts, the portion of the river downstream from our final effluent was designated a "Trophy Trout Stream". That is significant. When you have a rayon facility or any chemical operation that is able to put the water back in that it uses at a clean enough quality that trout, which is a particularly sensitive fish, can survive and, in fact, thrive. I think that speaks well of the job being done by our environmental people.

NASA and the Navy participated in the facilitization of the first machines, but then North American took it upon itself to get the financial backing to put the others one

in. We have done that and we are to the position now where we can produce more than 3 million pounds per year if need be. Therefore when we look ahead to those things that should be considered for protecting a program, what are you going to do to protect your individual program. We suggest that an alternative to the expense of testing and characterizing and qualifying somebody else for all these programs which would be very expensive would be to have us stockpile rayon in order to reduce the risk. The reasons that we think we can do it, we have the ability to stockpile. We have excess capacity here that is not being used. We also think that the money spent on tangible goods is more palatable to Congress, to everybody. When you spend your money on testing, you have no brick and mortar to show for it. We would offer to provide a two-year stockpile, maybe half for NASA and half for DOD and it would be a first in and first out situation. Therefore the age of the product would never be more than 2 years, but you would have 2 years worth and if we were to have an earthquake and drop down into the crevasse and were gone forever, you would have 2 years in which to find somebody else to do it. That is speaking to program protection.

Potential costs and liabilities in having two rayons segregated for traceability throughout each company in the chain, the weaver, the carbonizer, the prepregger, fabricator and so forth. That gets to be a bit of a chore to have everything segregated. I don't think you will end up having a generic rayon and a generic fabric. I think you will want to track this nozzle and that nozzle from the original source. If it is going to be source A, which would be us, and source B which would be somebody else, there can be costs and concerns with having to run segregated system. You all can best speak to that.

The implications of going away from a U.S. taxpaying corporation and its taxpaying employees would be unattractive to Congress. The inefficiency of dividing an already small market between two suppliers could result in a higher price, because it makes it less attractive and maybe less efficient of an operation by having the market divided among more than one.

In summary, North American believes that in view of the costs, the best approach is stockpiling and we know we are capable. Some considerations for potential long term development can include a water soluble finish. This was spoken to yesterday. We have the capability of providing you with samples or production size quantities. We stand ready to do that if we are asked to. We have some candidates in mind that would be tried, that we would recommend and then the carbonizers and weavers and so forth would have to test those and get back with us and say whether or not they performed up to standard. We can provide those at a nominal cost.

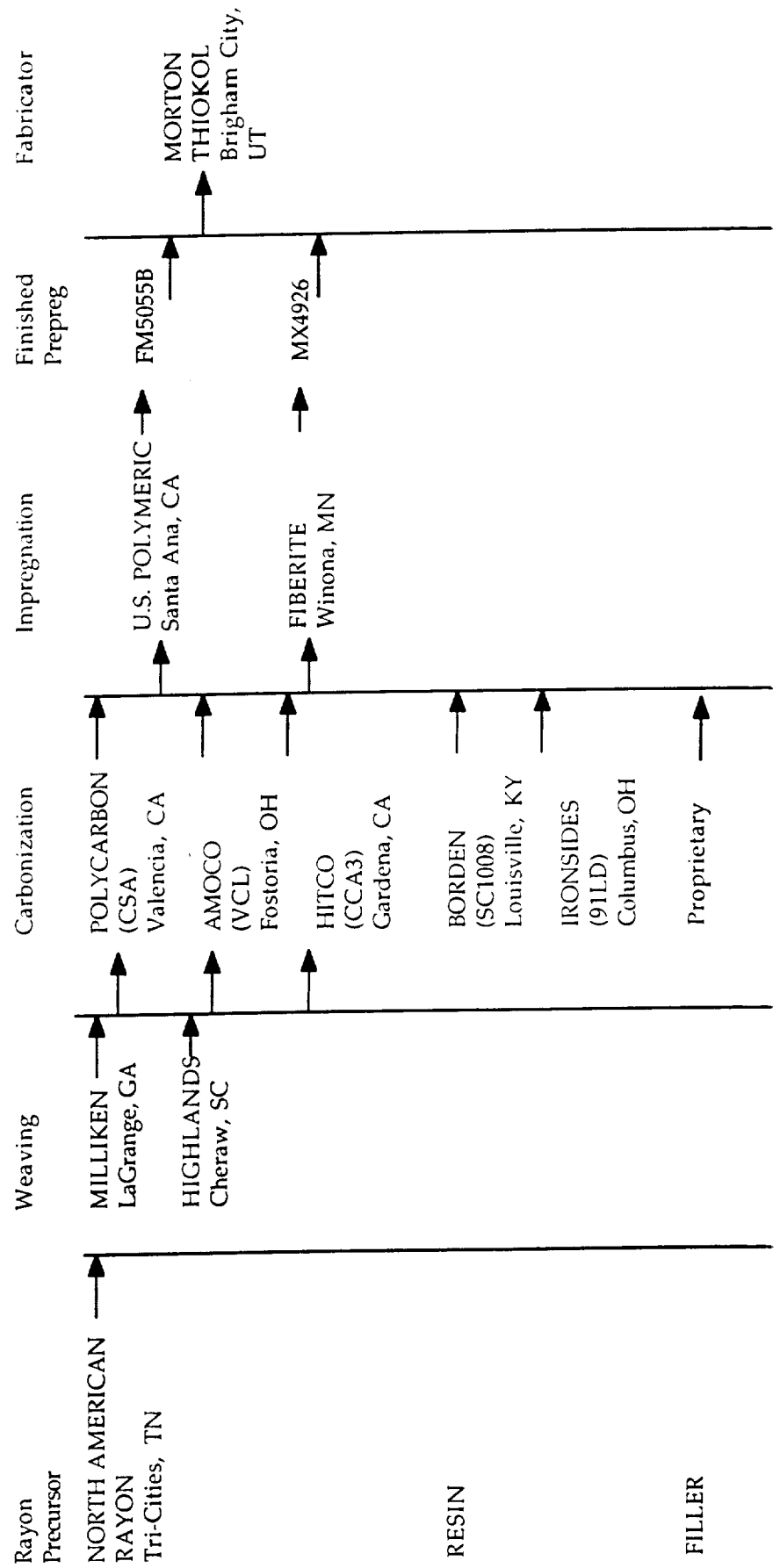
Yield improvement savings-If we were granted some expanded limits so that we didn't have to crowd the strength or the elongation edges, we would be willing to share in yield improvement which could result from that.

Carbon loading trials-I am not sure who thinks this is a worthwhile venture, but I know that in the past it has been spoken to for some years. The possibility of being able to increase carbon yield by injecting into the rayon process some ingredient, and we have about at least 3 or 4 candidates in mind that are potential improvements. We can do this. What I am saying is that we have the opportunity to inject ingredients into it in order to arrive in an improvement in yield. When we hear about all the development work that is going on with PAN and other items, we don't see why we shouldn't be involved in developing here, too. Rayon is a marvelously adaptable product and you can do many things with it that can change the entire characteristic and you can improve various things with manipulation of the chemistry. We offer that as a possibility for consideration. This concludes this part of the program. We are just trying to prove a point, to offer an alternative to what is going on.

APPENDIX A

WILLIAM B. HALL

Materials Supplier Flow Sheet for Carbon Phenolic Nozzle Components



APPENDIX B

ISMAIL ISMAIL

ASHING PROCEDURES AND ALKALI CONTENT OF CARBON FIBERS AND FABRICS

Ismail M. K. Ismail

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Outline

1. INTRODUCTION

- Does sodium influence nozzle erosion?
- Does sodium enhance oxidation rates?
- Why Na...How about others (K, Ca, ...)?

2. EXPERIMENTAL

- List of carbon fibers and fabrics examined
- Low temperature ashing
- High temperature ashing
- Summary of ASTM ashing tests

3. RESULTS ON HIGH TEMPERATURE ASHING

- WCA fabrics
- Low fired rayon fabrics
- Relations between Ash and Na content
- Influence of Na on enhancing oxidation rates

4. RESULTS ON LOW TEMPERATURE ASHING

- Exploring the experimental parameters
- LTA of WCA and CSA fabrics
- Titration of Ash/forms of Na

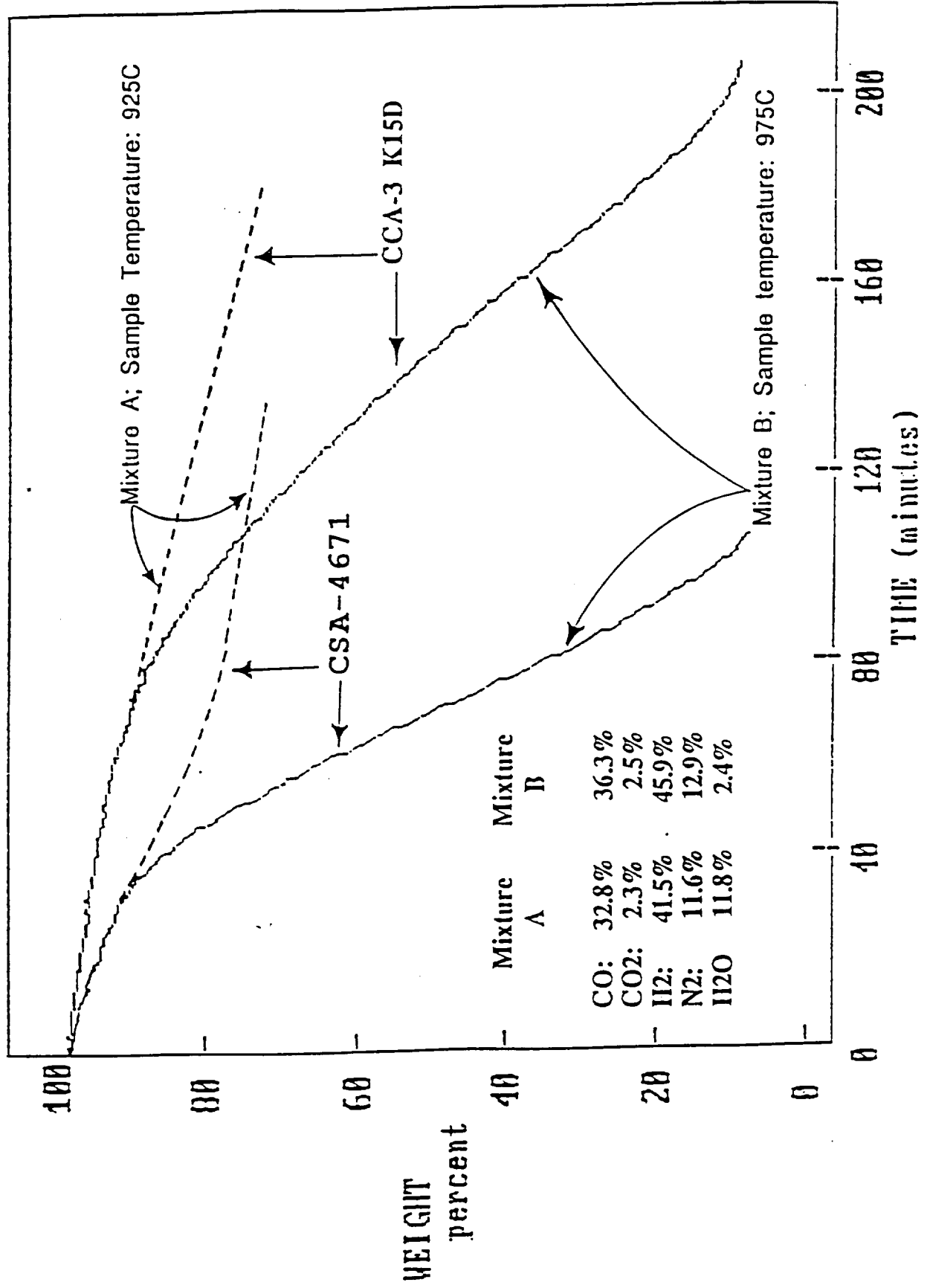
5. CONCLUSIONS

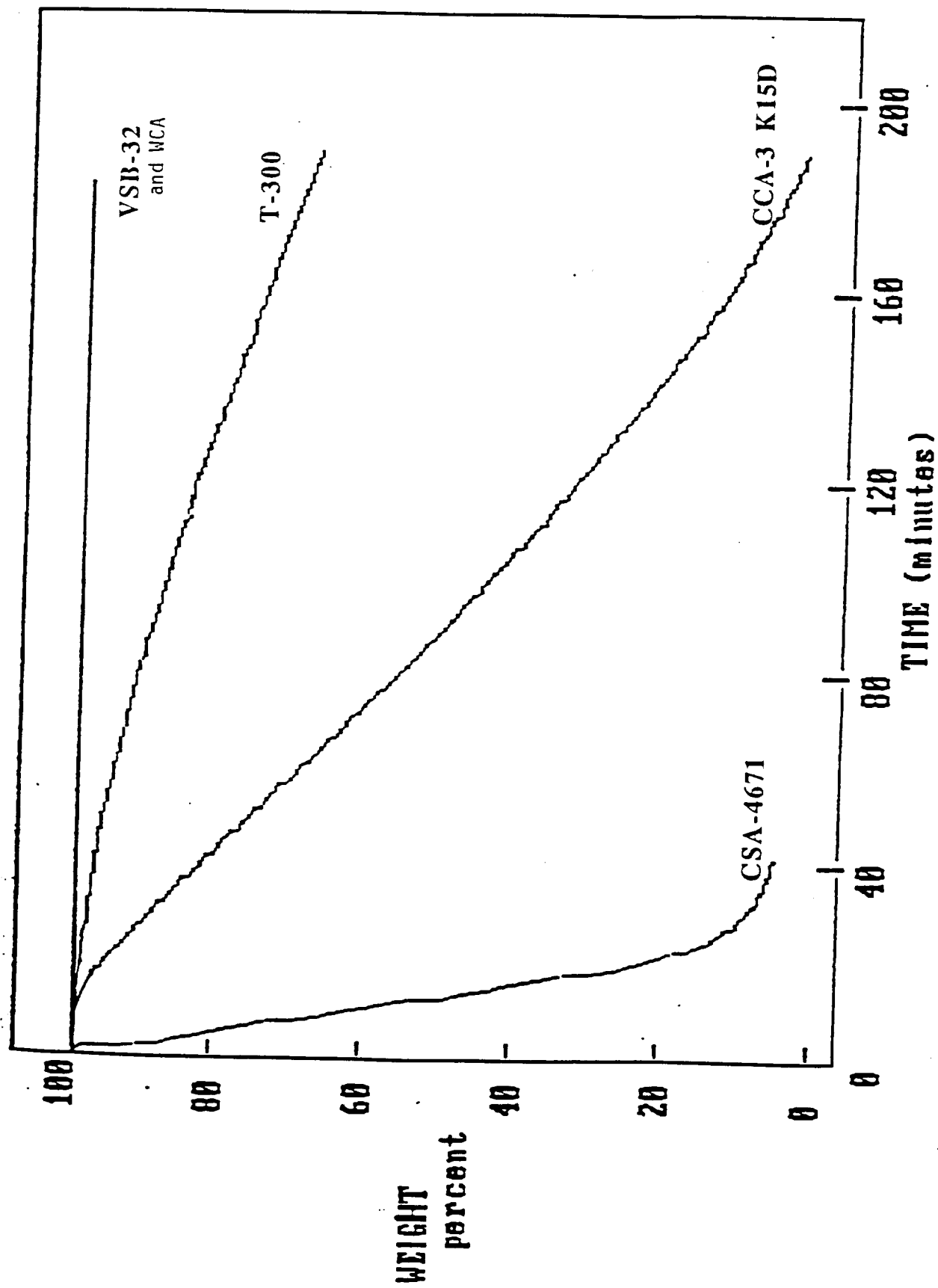
6. RECOMMENDATIONS

Materials Used for Space Transportation System (STS)

NOZZLE	STS-8A	STS-8B
Nozzle Erosion	Excessive	Nominal
Fabric used for the nozzle	<u>CSA-4671</u>	<u>CCA-3 KI5D</u>
BET Area (m ² /g)	0.48	0.81
Micropore area (m ² /g)	829	578
Micropore volume (cc/g)	0.337	0.235
Volume of Evolved Gases (cc/g)	30.1	20.3
Na (ppm)	<u>3153</u>	<u>170</u>
K (ppm)	110-199	38
Oxidation Rate at 500 C (mg/g/min)	75.0	6.0

RECESSION OF RAYON CARBON FABRICS IN SIMULATED ROCKET MOTOR EXHAUSTS FLOWING AT 100 cc/min





Oxidation of Carbon Fibers and Fabrics in Air at 500C.

List of Carbon Fibers and Fabrics Examined

NO.	MATERIAL	FORM	PRECURSOR	PROCESSING	REMARKS
1	T-300	Fiber	PAN	Carbonized	Similar to fabric used for STS-8A flight Similar to fabric used for STS-8B flight
2	VSB-32	Fiber	Pitch	Graphitized	
3	CSA-4671*	Fabric	Rayon	Carbonized	Rack (discoloration) bands
4	CCA-3 K15D**	Fabric	Rayon	Carbonized	
5	WCA-1	Fabric	Rayon	Graphitized	NASA (Lot number CO 2018-1)
6	WCA-2	Fabric	Rayon	Graphitized	
7	WCA-3	Fabric	Rayon	Graphitized	1986 Fiberite production, Roll #343 AFAL Roll #888
8	WCA-4	Fabric	Rayon	Graphitized	
9	WCA-5	Fabric	Rayon	Graphitized	
10	WCA-6	Fabric	Rayon	Graphitized	
11	WCA-7	Fabric	Rayon	Graphitized	
12	WCA-8	Fabric	Rayon	Graphitized	
13	WCA-9	Fabric	Rayon	Graphitized	
14	WCA-10	Fabric	Rayon	Graphitized	
15	WCA-11	Fabric	Rayon	Graphitized	
16	WCA-12	Fabric	Rayon	Graphitized	
17	WCA-13	Fabric	Rayon	Graphitized	
18	WCA-14	Fabric	Rayon	Graphitized	
19	WCA-15	Fabric	Rayon	Graphitized	

* Represents the fabric used to manufacture the suspect STS-8A nozzle component (excessive erosion)

** Represents the fabric used to manufacture STS-8B nozzle component (nominal erosion)

LIST OF CARBON FIBERS AND FABRICS EXAMINED
(cont'd)

No.	Sample	Form	Precursor	Processing	Manufacturer
20	CSA (lot 4721)	Fabric	Rayon	Carbonized	Polycarbon Inc.
21	CSA (lot 64012A)	Fabric	Rayon	Carbonized	Polycarbon Inc.
22	CCA-3 1641B	Fabric	Rayon	Carbonized	Hitco
23	CCA-3 roll 3	Fabric	Rayon	Carbonized	Hitco
24	CCA-3 roll 2	Fabric	Rayon	Carbonized	Hitco
25	CCA-3 roll 1	Fabric	Rayon	Carbonized	Hitco
26	VCL roll 95	Fabric	Rayon	Carbonized	Union Carbide
27	VCK roll 210	Fabric	Rayon	Carbonized	Union Carbide
28	VCL roll 273	Fabric	Rayon	Carbonized	Union Carbide
29	CSA-5339	Fabric	Rayon	Carbonized	Polycarbon Inc.
30	CSA-5375	Fabric	Rayon	Carbonized	Polycarbon Inc.

Summary of ASTM Ashing Tests

Material	ASTM Designation	Sample wt. (g)	Ashing Temp. (C)	Preheated Oven (Y/N)	Ashing Time	Remarks	Repeatability (single Operator)	Reproducibility (Multi Lab)
Carbon Black	D1506-85	2.0 (dry)	550 ↗ 950	yes yes	16 h 4-5 h	uncovered permissible	20%	23%
Activated Carbon	D2866-83	Sufficient to yield 0.1 ash	650 ± 25	yes	3-16 h	constant weight achieved	being investigated	being investigated
Graphite	C561-69	?	500 ↗ 750 950 ↗	no	1 h 2 h 1 h	Platinum dish (250 µm)	being developed	being developed
Coal & Coke	D3174-82	1.0	450-500 700-750	no	1 h 2 h/or more	Capsule/ Porcelain or Platinum cover	0.2-0.3%	0.3-0.5%
Petroleum Coke	D4422-84	10.0*	700-750	no	until constant mass	<75µ	0.02 (%)?	0.06 (%)?
Graphite lubricants	D1553-83	1.0 (dry)	950±25	yes	3 h	Capsule < 1 mg loss in 1/2 h	0.15%	0.22%

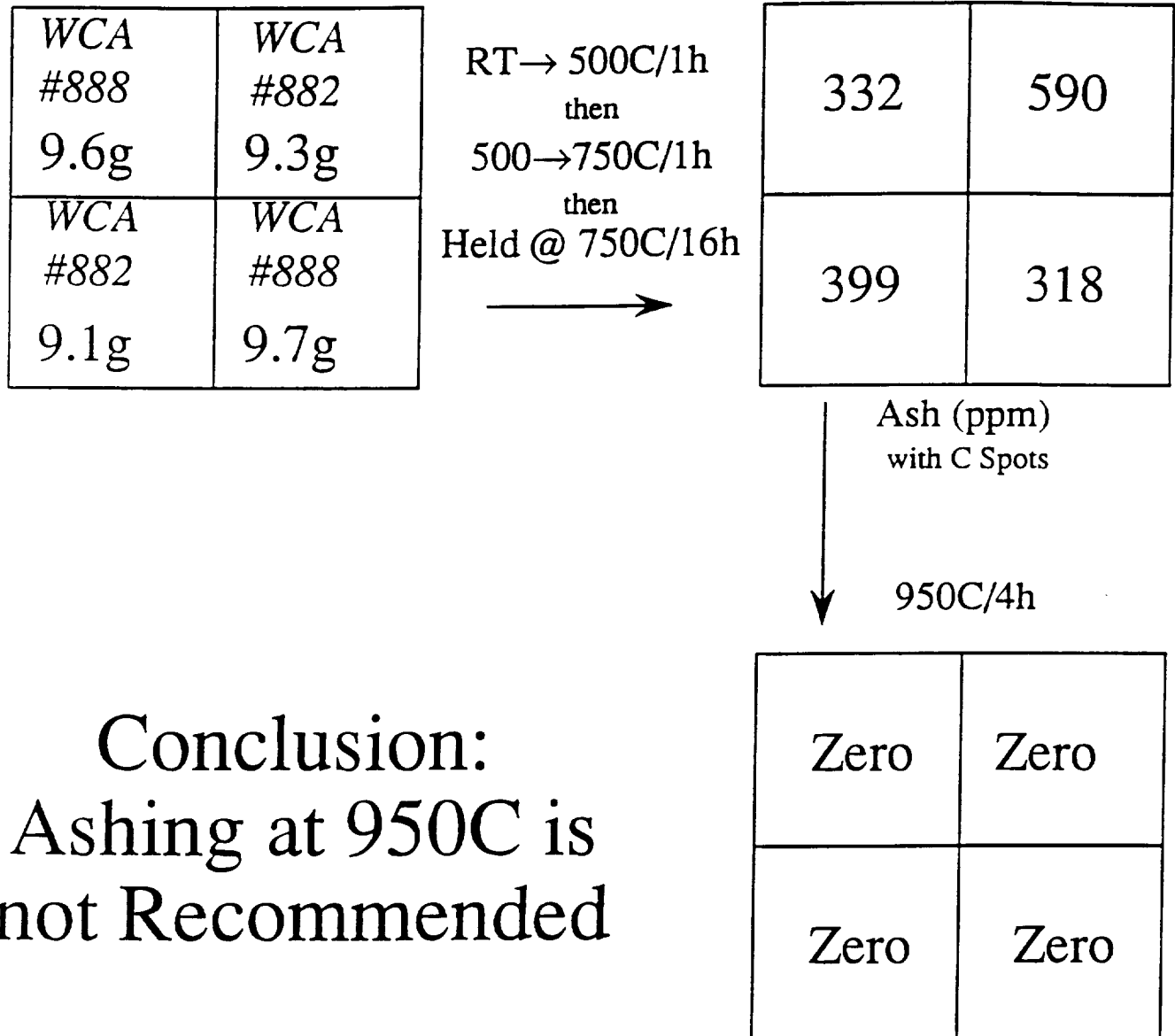
*ASTM: 10 ± 0.1 mg (Typo?)

Ashing temperature (t) and time (t)

Condition	Result	Ash Content
Low T, short t	Ashing is incomplete	Over estimated
High T, short t	Ashing is complete	May be acceptable or underestimated
Low T, long t	Ashing is probably complete	May be acceptable, underestimated, or over estimated
High T, long t	Ash may evaporate	Underestimated

ASTM:	Lowest temperature - 550 C	<u>Melting Points:</u>
	Highest temperature - 950 C	N ₂ CO ₃ : 851 C
ASTM time:	Shortest time - 1 hour	Na ₂ SO ₄ : 884 C
	Longest time - until a constant weight is reached	

High Temperature Ashing of Two WCA Fabrics



High Temperature Ashing of two WCA Fabrics

WCA	#888	7.2g	WCA	#882	6.2g
WCA	#882	7.8g	WCA	#888	7.6g

RT → 500C/1h
then
500 → 750C/1h
then
Hold @ 750C/3h

216	263
289	172

Ash (ppm)
with C Spots

750C/21h

51	64
44	31

White Ash(ppm)

750C/24h

62	77
115	62

Ash (ppm)
with
one C spot

FABRIC	SURFACE AREA (a)	ALKALI CONCENTRATION (b)		PYROLYSIS YIELD (cc/g @ STP)	OXIDATION RATE (c) (mg/g/min)
		Na (ppm)	K (ppm)		
WCA-1	1.00	5.0	4.5	0.18	2.73
WCA-2*	0.88	5.2	3.3	0.12	2.69
WCA-3	0.66	6.9	2.4	0.25	2.70
WCA-4	0.72	1.4	1.1	0.23	2.76
WCA-5**	0.74	<0.1	<0.1	0.23	3.01
WCA-6	0.75	1.0	<0.1	0.17	3.13
WCA-7	0.76	<0.1	<0.1	0.21	2.73
WCA-8	0.78	0.3	<0.1	0.15	3.16
WCA-9	N/A (d)	12.3	8.1	0.23	3.19
WCA-10	0.66	<0.1	<0.1	N/A	3.34
WCA-11	0.62	1.5	2.0	N/A	3.27
WCA-12	0.61	2.3	4.2	0.13	2.91
WCA-13	0.60	6.3	3.1	0.14	2.83
WCA-14	0.65	<0.1	<0.1	0.13	2.91

* having rack bands

(a) From Kr adsorption at -196 K.

(b) Concentration of Cr was <0.1 ppm for all samples.

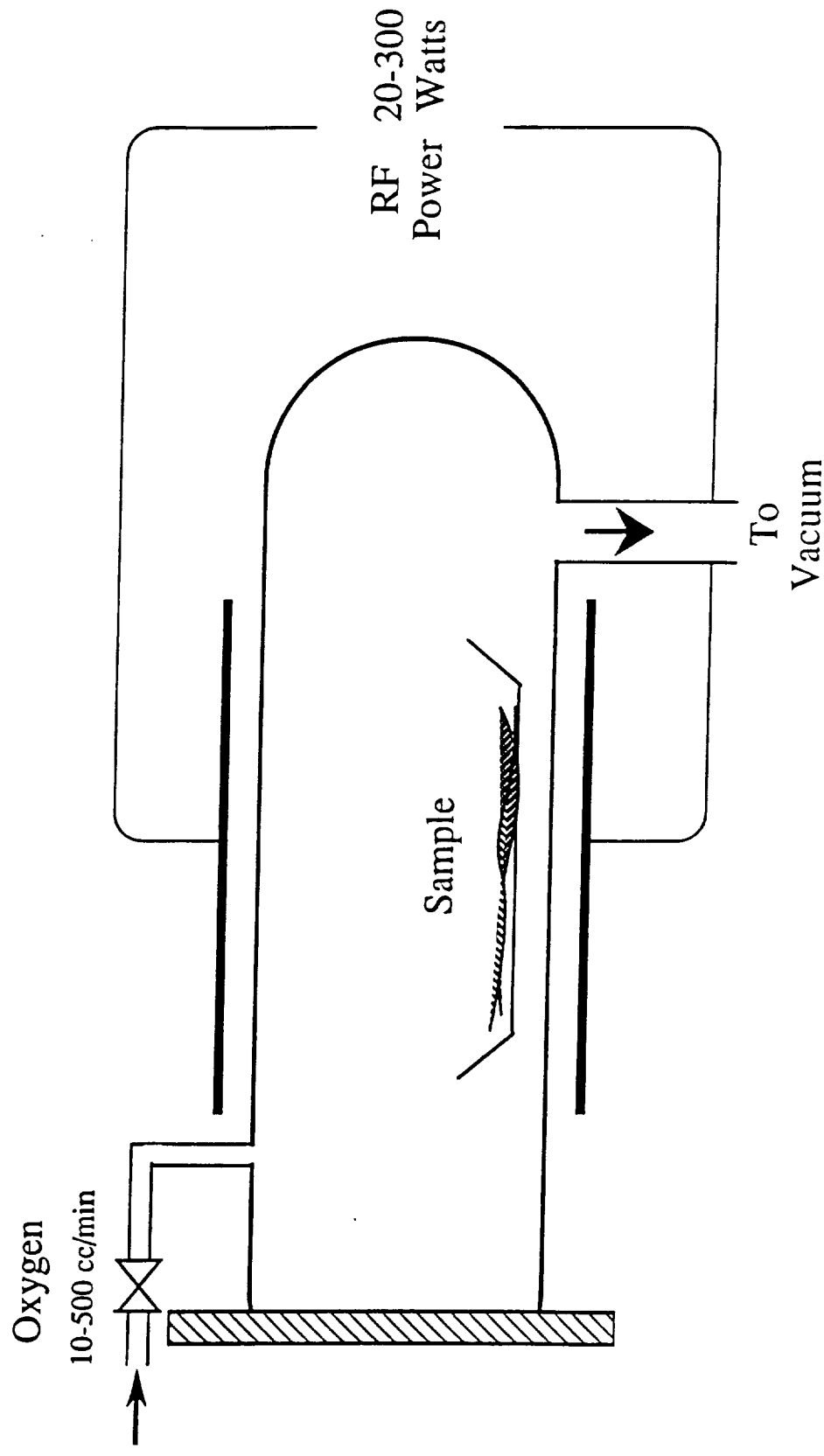
(c) Rates measured in air at 700 C and 50% burn-off.

(d) Not available

**NASA Fabric: poor mechanical properties

***Ash Content of all WCA samples: 0.01-0.09.

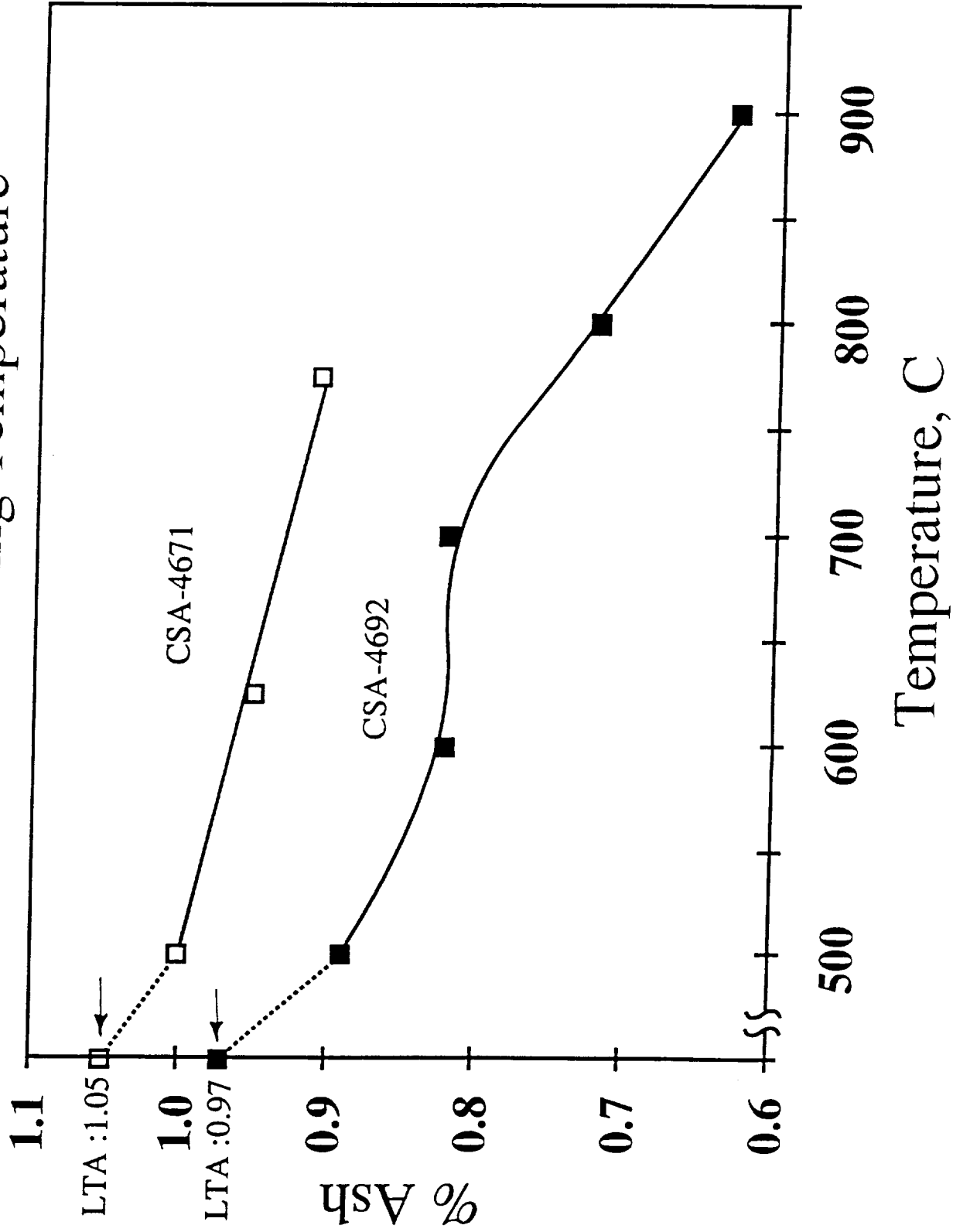
Low Temperature Ashing using Oxygen plasma (Branson, IPC model S3003)



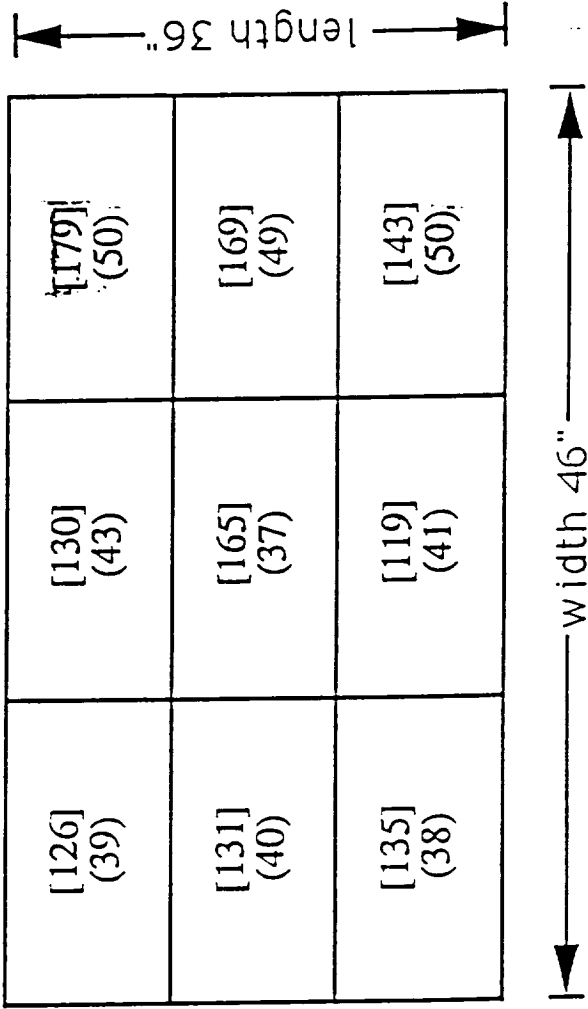
MATERIAL	LOW TEMPERATURE ASH, %	HIGH TEMPERATURE ASHING	
		ASH TEMPERATURE	ASH, %
CSA-4671	1.049	625 C	0.95 -
		500 C(a)	1.05 ± 0.05
		500 C(b)	1.009
WCA-15	0.069	950 C	0.000
		750 C (c)	0.032
		750 C (d)	0.004
WCA-14	0.080 ± .005 (e)	650 (f)	0.070

- (a) Small Sample (1.0 g)
 (b) Large Sample (7.0 g)
 (c) Overnight at 750 C
 (d) 61 hours at 750 C
 (e) Average of three runs (25.0 g each)
 (f) 61 hours at 650 C

Effect of Ashing Temperature



Distribution of Na and K along CSA-64012A Fabric



Alkali Contents of Carbon Fibers and Fabrics

#	Material	Ash (%)	Na (ppm)	Ash (Normalized)	Na (Normalized)
1	T-300 AR	0.09	11.3	9	6.2
2	T-300 GR	0.08	2.3	8	1.3
3	VSF-32 AR	0.05	4.4	5	2.4
4	VSF-32 GR	0.02	1.8	2	1.0
5	WCA	0.01-0.09	0.1-12.3*	1-5	0-7.0
6	CSA (lot 4671)	1.0	3153	100	1752
7	CSA (lot 4721)	0.30	824	30	458
8	CSA (lot 64012A)	0.18	144	18	80
9	CCA-3 K15D	0.22	170	22	94.4
10	CCA-3 1641B	0.02	13	2	7.2
11	CCA-3 roll 3	0.3	468	30	260
12	CCA-3 roll 2	0.3	577	30	320.6
13	CCA-3 roll 1	0.6	1704	60	946.7
14	VCL roll 95	0.54	1459	21	810.6
15	VCK roll 210	N/A*	583	N/A	323.9
16	VCL roll 273	0.3	526	30	292.2

* Not available

Removal of Alkali Contents of CSA- 4671 by washing

WASHING MEDIUM	DD WATER		HCl		HNO ₃	
Constituent	Na	K	Na	K	Na	K
Concentration (ppm):						
Filtrate	1379	13.3	1562	42.3	1769	N/D*
Fabric	1773	69.4	1591	68.0	N/A**	N/A**
Total	3152	82.7	3153	110.3		

* Not detected

** Not available

DISTRIBUTION OF SODIUM IN CSA-4671 FABRIC:

- 43.7% WATER SOLUBLE SALT(S)

- 5.8% CHEMICALLY BONDED TO FUNCTIONAL GROUPS
AT EXTERNAL SURFACE

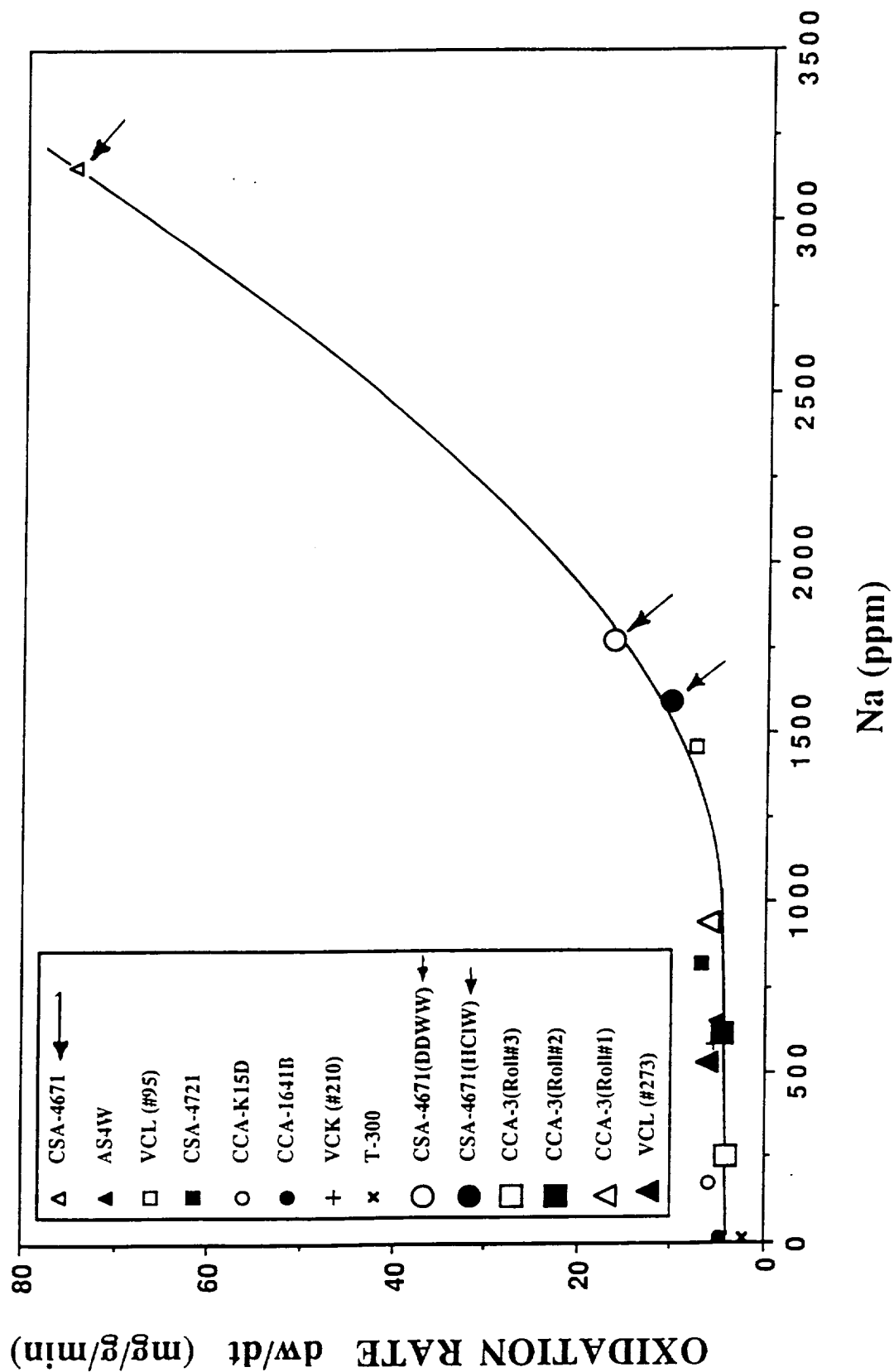
- 50.5% TRAPPED INSIDE PORES (as Salts or Chemically Bonded)

TOTAL 100.0%

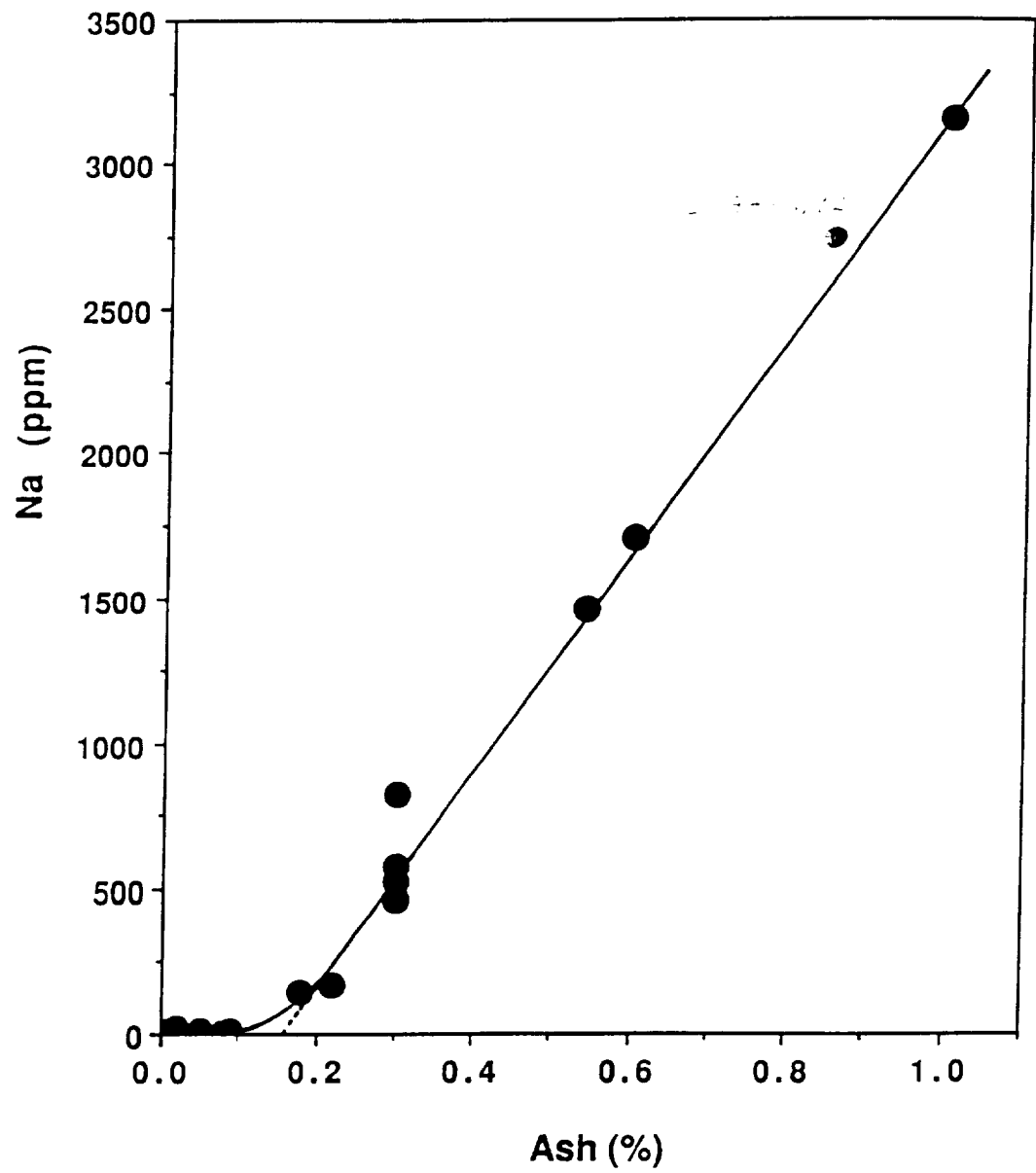
**84%
SULFATE**

**16%
OTHERS
(Carbonates?)**

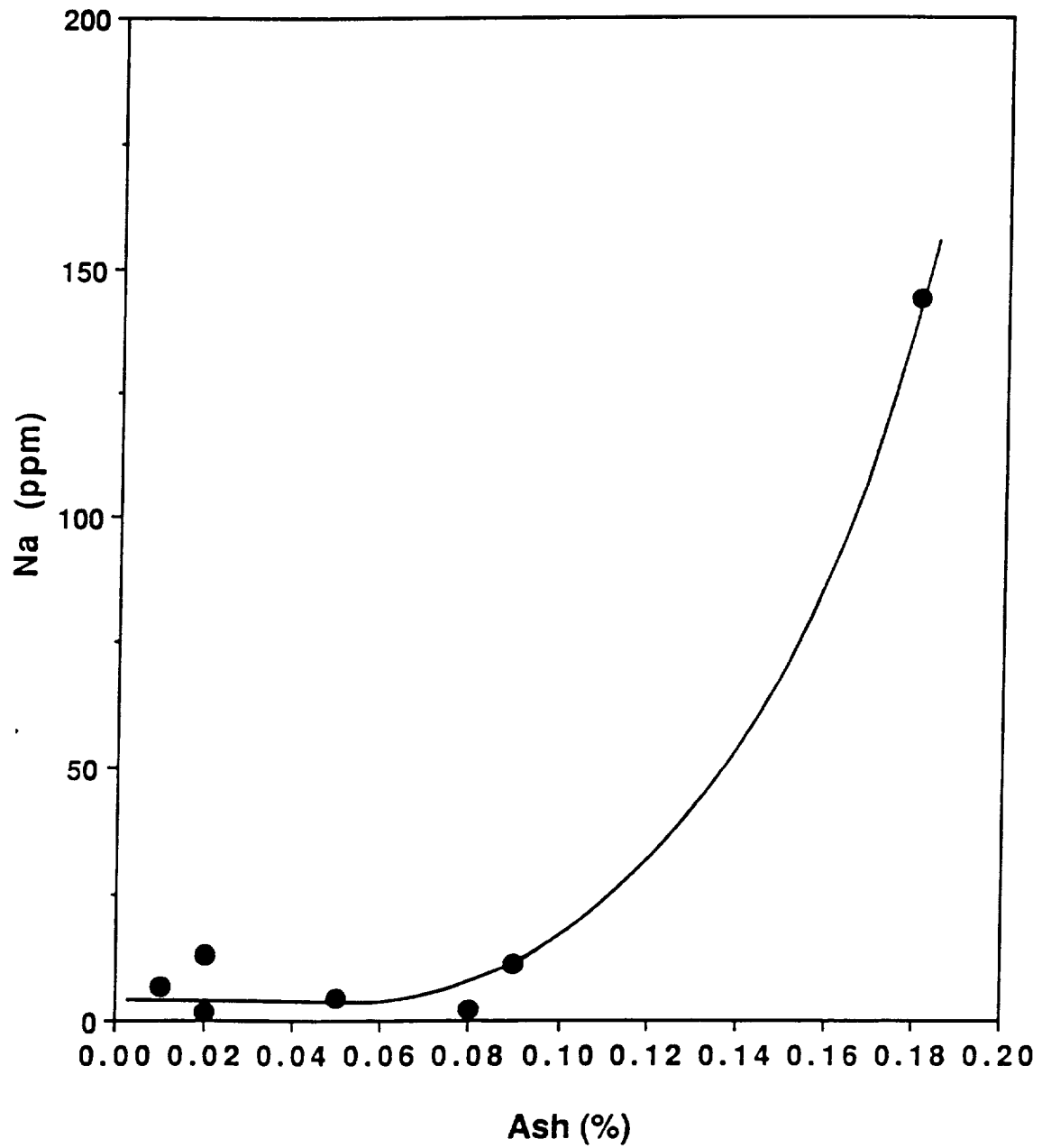
Dependence of Oxidation Rate at 500 C on the Sodium Concentration in Fibers and Fabrics



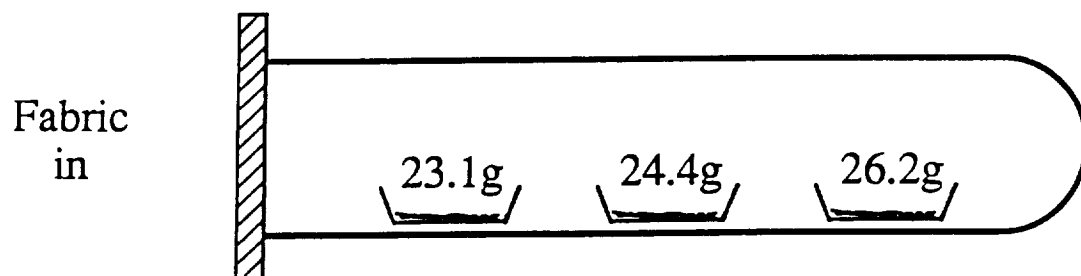
Relation Between Ash and Na Content



Relation Between Ash and Na Content



Low Temperature Ashing WCA (Fiberite) Fabric



Oxygen Flow : 300 cc/min
RF Power : 240 Watts
Time : 65 h

Residue(ppm) 1505 7671 3093
Ash+black spots

300 cc/min
240 Watts
22 h

Residue(ppm) 835 937 833
All white Some black All white

500 cc/min
280 Watts
29 h

Residue(ppm) 757 846 777
All white All white All white

Average Ash Content = 839 ± 7 ppm
= 0.084%

LOW TEMPERATURE ASHING OF WCA #888

Starting weight of fabric = 35.9076 g

Power (Watt)	O ₂ Flow Rate	Oxidation Time	Residue
280	100 cc/min	5 h	22.2 g
200	100 cc/min	19 h	
240	300 cc/min	25 h	752 ppm (one black spot)
200	300 cc/min	70 h	713 ppm white ←
240	300 cc/min	18 h	696 ppm white

LOW TEMPERATURE ASHING OF CSA-4692

Starting weight: 10.0217 g

Power: 50 Watt

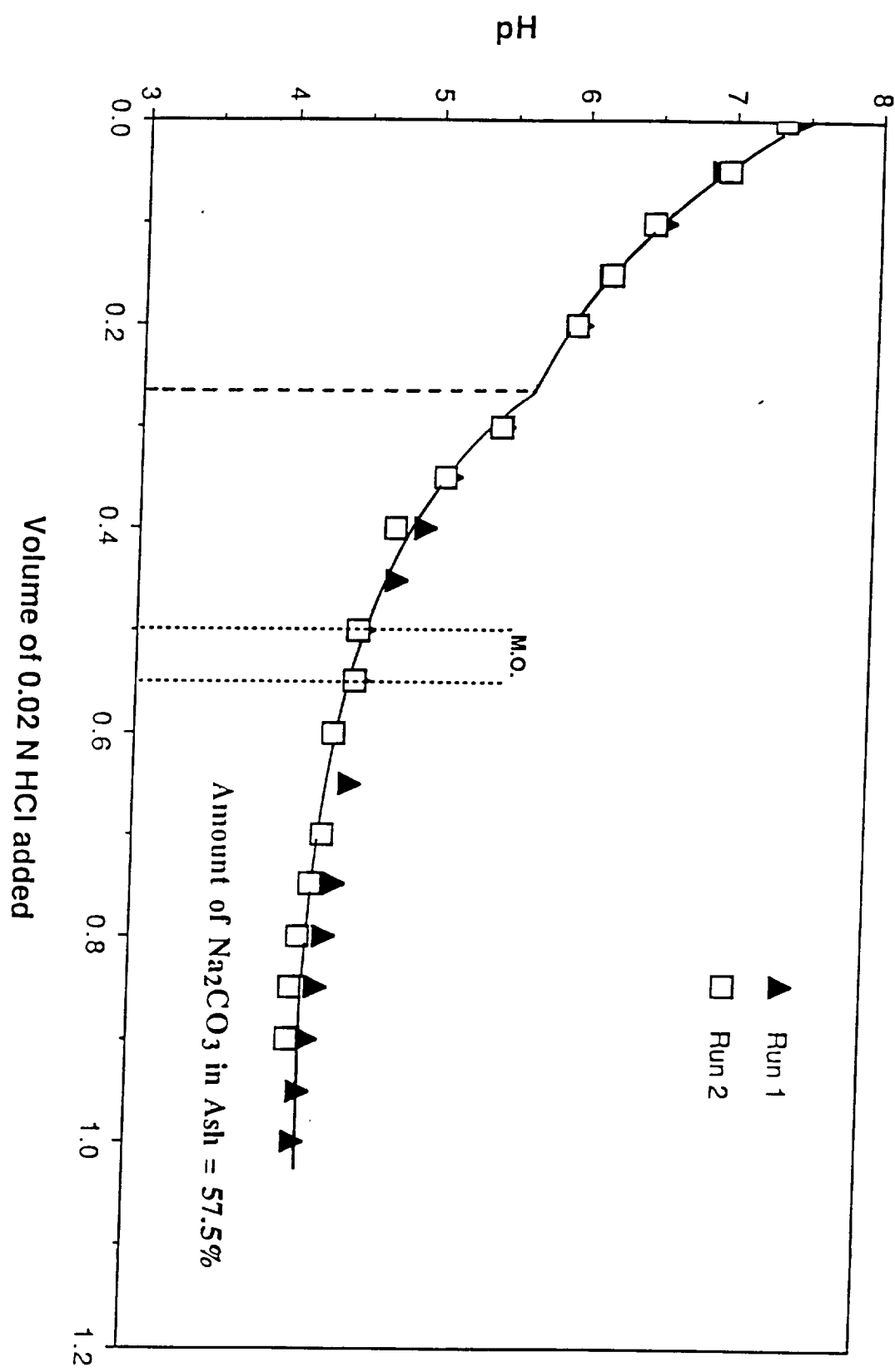
O₂ Flow Rate: 50 cc/min

Oxidation Time: 7 days

% Ash = 0.971 all white

High temperature oxidation at 500 C → 0.89%

Titration of Low Temperature Ash Solution Obtained From CSA-4692 Against HCl



CONCLUSIONS

- Ashing Rayon fabrics at 950 C underestimates the ash content; it may yield 0% Ash.
- Ashing of the fabrics at 750 C for longer periods of time, > 3 hours, underestimates the Ash content.
- Ashing temperature of carbon fibers and fabrics should be at 500-600 C; depending on the material.
- Low temperature ashing is an attractive alternative.
- With low fired Rayon fabrics most of the sodium is present as Na_2CO_3 and Na_2SO_4 .

RECOMMENDATIONS

- **Proposed Ashing Temperature for low fired Rayon fabrics: 500-550 C.**
- **Proposed Ashing Temperature for high fired Rayon fabrics (e.g., WCA): 550-600 C.**
- **Low Temperature Ashing in an oxygen plasma is recommend, if the equipment is available.**

APPENDIX C

PAT C. PINOLI

NASA/SPIP PRODUCT CODE IDENTIFICATION

PRODUCT IDENTIFICATION

- SUBCOMMITTEE IDENTIFIED TWO PRODUCTS FOR IMMEDIATE ATTENTION
 - CARBON FABRIC
 - PRE-PREG

NASA/SPIP PRODUCT CODE IDENTIFICATION

CARBON FIBER IDENTIFICATION CONSIDERATION

- PRECURSOR TYPE
- PRECURSOR SOURCE
- PRECURSOR YARN DENIER/FILAMENT COUNT
- PREWOVEN/POST WOVEN
- FABRIC CONSTRUCTION
- FABRIC FIRING TEMPERATURE
- MOISTURE ADSORPTION CAPACITY
- ELECTRICAL RESISTIVITY

NASA/SPIP PRODUCT CODE IDENTIFICATION

CARBON FIBER CODE RECOMMENDATIONS

- | | |
|---|--|
| 1. PRECURSOR TYPE | 4. PREWOVEN OR POST WOVEN |
| R RAYON | A PREWOVEN |
| P PAN | B POST WOVEN |
| M PITCH (MEZOPHASE) | |
| 2. PRECURSOR SOURCE | 5. FABRIC WEAVE |
| A AVTEX | 5HS 5 HARNAUS |
| N NORTH AMERICAN RAYON | 8HS 8 HARNAUS |
| G GRUPO CYDSA | PL PLAIN |
| O UNKNOWN, NOT SPECIFIED | NO UNKNOWN, NOT SPECIFIED |
| 3. PRECURSOR YARN DENIER/FILAMENT COUNT | 6. FABRIC FIRING TEMPERATURE |
| 11 11100 DENIER | 0-16 MOISTURE ADSORPTION CAPACITY, MAXIMUM |
| 16 1650 DENIER | 35-70 ELECTRICAL RESISTIVITY, U OHM-M, MINIMUM |
| K FILAMENT COUNT | |

SAMPLE CODES FOR:

- ASRM FIBER, INITIAL SPECIFICATION
SPIF R/N/16/A&B/MC/012/00

NASA/SPIP PRODUCT CODE IDENTIFICATION

PREPREG IDENTIFICATION CONSIDERATION

- CARBON FIBER CODE ON UPPER LINE
- THERMOSET RESIN
- FILLED/UNFILLED
- FILLER CONTENT, W%
- FILLER TYPE
- SOLUTION/HOT MELT

**SPIP - CARBON ASSAY TESTING CALIBRATION
ROUND ROBIN TEST RESULTS
(502-099/191-A-L)⁽¹⁾**

LABORATORY

RUN	A	B	C
1	95.2	97.05	95.98
2	95.2	97.22	96.12
3	95.2	97.08	96.42
4	95.3		96.18
5	95.6		96.89
X	95.3	97.12	96.32
S	0.17	0.09	0.36

(1) NBS Carbon Assay 96.81 = 0.38

DEVELOPMENT OF LOW-THERMAL-CONDUCTIVITY PAN-BASED FIBERS FOR SOLID ROCKET NOZZLE APPLICATION*

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**Thiokol Corporation, Brigham City, Utah

ABSTRACT

The NASA-sponsored Solid Propulsion Integrity Program (SPIP) has initiated an effort to evaluate eight low-conductivity polyacrylonitrile (PAN)-based fiber candidates as potential replacements for traditional rayon-based fiber in ablative applications. These candidates were manufactured from commercial precursor PAN fiber by Amoco, Hercules, Textron, and BASF Celanese. An extensive fiber-characterization program was conducted to measure the properties of fibers from all sources at one test facility and to assess the relationship of fiber properties to prepreg processing characteristics and to subscale test performance. Low fiber thermal conductivity (measured by electrical resistivity) was established as the primary discriminator for this effort. The eight candidate PAN-based 3 K yarns were submitted for evaluation prior to postweaving into 5 H.S. fabric. The electrical resistivities ranged from 27 to over 60,000 $\mu\Omega\cdot\text{m}$. Current production lots of conventional shuttle-grade rayon-based fabrics (CSA/CCA3 and VCL) have electrical resistivities from 45 to 55 $\mu\Omega\cdot\text{m}$. Other fiber properties measured were: density, moisture adsorption capacity, isopropanol adsorption capacity, alkaline metal content, sodium equivalents, oxidation rate, carbon assay, ash content, tensile strength, tensile modulus, strain-to-failure, and the effect of high-temperature heat treatment (2500°C).

The properties of low-conductivity PAN fibers are summarized and reviewed. Subscale testing of the eight PAN fiber variations is currently in progress at Thiokol Corporation, Brigham City, Utah. Erosion profile and char depth data will be presented at the conference.

INTRODUCTION

Rayon-based carbon fiber is traditionally used by the aerospace industry for ablative applications. The major advantage of rayon-based fiber is its intrinsically low thermal conductivity. The sole domestic supplier of carbonizable rayon, Avtex, at Front Royal, Virginia, went out of business in 1989. The continued declining market for continuous filament rayon and the environmental issues related to fiber manufacturing have induced the aerospace industry to explore alternative carbon fibers for ablative applications. The predominant commercial carbon fiber today is PAN-based fiber, for which demand is increasing and cost projections are declining.

Commercial PAN-based fiber is designed to meet the requirements of structural composites, which are generally tensile and modulus driven. Carbon fibers used in ablative applications are unusual in that their design requirements are not generally driven by structural-property requirements. Ablative applications require low-thermal-conductivity fiber to minimize char depth and backside temperature rise.¹

This program was initiated to determine the potential for achieving ablative-level fiber thermal properties with current high-production PAN precursor. It is sponsored by NASA's Solid Propulsion Integrity Program (SPIP).

PROGRAM OVERVIEW

As the first step in this program, all of the major domestic suppliers of PAN-based fibers were queried for interest in a program designed to assess the potential of low-conductivity PAN-based fiber for ablative application. The fiber property goals presented to the suppliers were as shown in Table I. Issues agreed upon by general consensus with the suppliers to ensure a fair evaluation of each vendor's products are shown in Table II. The suppliers who submitted products for evaluation are listed in Table III, along with their fiber codes.

Each supplier was permitted to submit two 3 K yarn variations for initial Phase I evaluation, as shown in Fig. 1. To achieve lower thermal conductivity, the firing temperature of candidate PAN-based fibers was reduced to around 1000°C. The fiber suppliers used standard commercial PAN precursor to produce eight variations of 3 K yarn with low thermal conductivity. These eight variations were postwoven into 5 H.S. fabric, prepregged, and subscale tested under Phase I of this effort.

*This work was performed under Contract No. NAS8-37801 (via Subcontract P.O. 1157-03009 with Hercules Aerospace Co.) as part of NASA's Solid Propulsion Integrity Program. This document contains information which falls under the purview of the U.S. Munitions List, as defined in the International Traffic in Arms Regulations. It shall not be transferred to foreign nationals, in the U.S. or abroad, without specific approval. Penalty for violations is described in ITAR, Section 127. Distribution authorized to U.S. Government agencies and U.S. Government agency contractors ONLY. Other requests for this document shall be referred to NASA, MSFC, ER41/Solid Propulsion Research & Technology Office.

Table I LOW-THERMAL-CONDUCTIVITY PAN-BASED FIBER PROPERTY GOALS

Priority	Fiber Property	Desired Level	Minimum Properties
•	Electrical Resistivity	> 70 $\mu\Omega\text{-m}$	50 $\mu\Omega\text{-m}$
Identified Significant Characteristics			
	Oxidation Rate	\leq Rayon	Zone 1 air oxidation rate lower than rayon
	Alkali Metal Content	Ultrapure precursor	1000 ppm of Na equivalents
	Moisture Adsorption Capacity	Low	< 6 wt %
	Density	< 1.50 g/cm ³	< 1.80 g/cm ³
	Thermal Shrinkage (to 2500°C)	Low	< 2%
	Carbon Assay	High	80 wt %
	Tensile Strength	High	> 200 ksi
	Tensile Modulus	Low	< 30 msi

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Table II LOW-THERMAL-CONDUCTIVITY PAN-BASED FIBER PROGRAM REQUIREMENTS

Issue	Program Requirements
1. Yarn Tow Size	3 K for all suppliers
2. Yarn Form	Only continuous filament
3. Lot Production Time	8 weeks after receipt of order
4. Lot Production Quantity	20 lb
5. Sizing	Phenolic compatible
6. PAN Precursor	Standard vendor precursor
7. Twist	No twist
8. Broadgoods Weave	Postwoven 5 H.S.
9. Spool Type	Weaver to specify
10. Weaver	Ketema, Textile Products Div.
11. Prepregger	ICI/Fiberte by wet dip
12. Resin	SC-1008

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Table III PHASE I YARN SUPPLIERS AND PRODUCT CODES

PAN-Based Yarn Supplier	Product Code
Amoco Performance Products, Inc.	T-350/23 x AB T-350/25 x AB
BASF Structural Materials, Inc. (Celanese)	DG Rayon 2 DG Rayon 1
Hercules Graphite Fibers	R879-01 (with sizing-03) R879-02 (with sizing-04)
Textron Specialty Materials	Avcarb G Avcarb B-2

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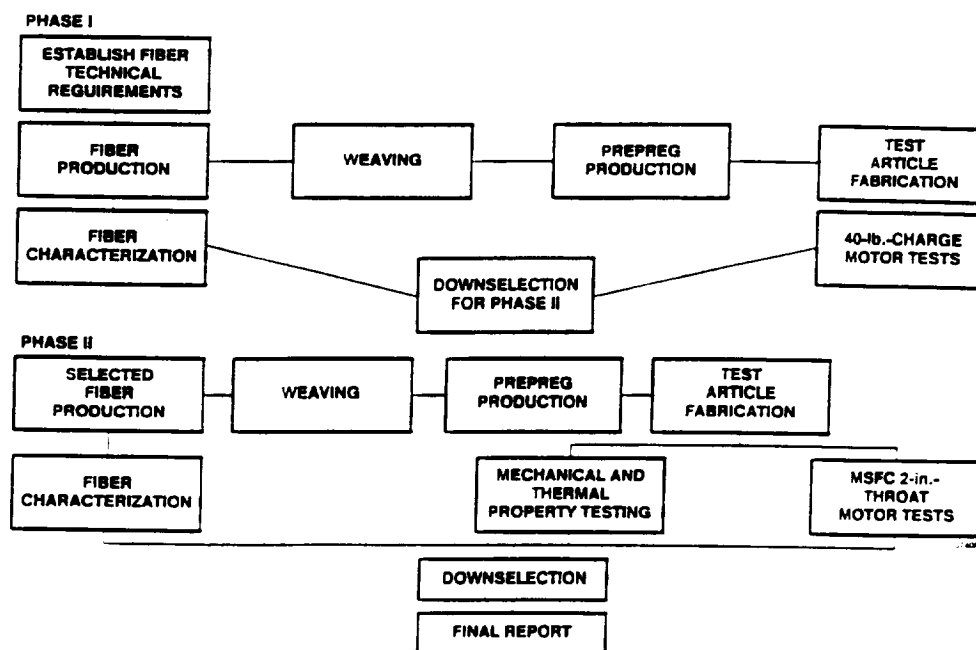


Fig. 1 Program Plan for Development of Low-Thermal-Conductivity PAN-Based Carbon Fibers

Phase I of the program was designed to fully characterize the eight candidate yarns and to evaluate their performance with 40-lb-charge motors at Thiokol Corporation, Brigham City, Utah. This preliminary screening effort is designed to reduce the number of fiber candidates to five for more intensive assessment in Phase II. The Phase II assessment will utilize knowledge gained in Phase I regarding fiber testing methodology, prepreg processing, test article fabrication, and subscale test evaluation.

The next section presents fiber characterization data generated by common test technique. It is followed by a section presenting the subscale test evaluation data from the 40-lb-charge motor firings.

FIBER CHARACTERIZATION

The properties of the eight candidate PAN-based yarns were measured at the Lockheed Palo Alto Research Laboratory (LPARL) using the same test techniques for all candidates. Analysis by a single test facility was introduced because many diverse test techniques are used by the manufacturers and end users. In addition, an independent laboratory was used, since some of the test requirements were not familiar to the manufacturers. Recent studies on rayon-based fiber and previous work on low-conductivity PAN have identified many new fiber characteristics of interest.²⁻⁸ These new characteristics do not have defined limits, and the relationship of fiber properties to performance has not been established. The fiber characterization effort therefore included a study of testing methodology, establishment of comparative properties for rayon-based fibers, and the testing of candidate PAN-based fibers.

The following subsections discuss test methodology and the results of fiber characterization.

ELECTRICAL RESISTIVITY

The thermal conductivity of carbon products is usually assessed by direct measurement of electrical resistivity. The relationship of the thermal conductivity of carbon fiber to its electrical resistivity has been extensively documented by Amoco and is presented in Fig. 2. This program adopted the standard Amoco procedure, four-point resistance at 50- and 100-cm yarn lengths, which follows the general guidelines of ASTM D3800 and D4018. Measurement of fiber electrical resistivity involves direct measurement of tow resistance (Ω /cm), yarn yield (g/cm), and fiber density (g/cm^3). A constant, $k = 10^4$, is used to convert the measured resistivity to micro-ohm meters ($\mu\Omega\text{-m}$).

$$\text{Electrical Resistivity} = \frac{\text{Resistance} \times \text{Yield}}{\text{Density}} \cdot k \quad (1)$$

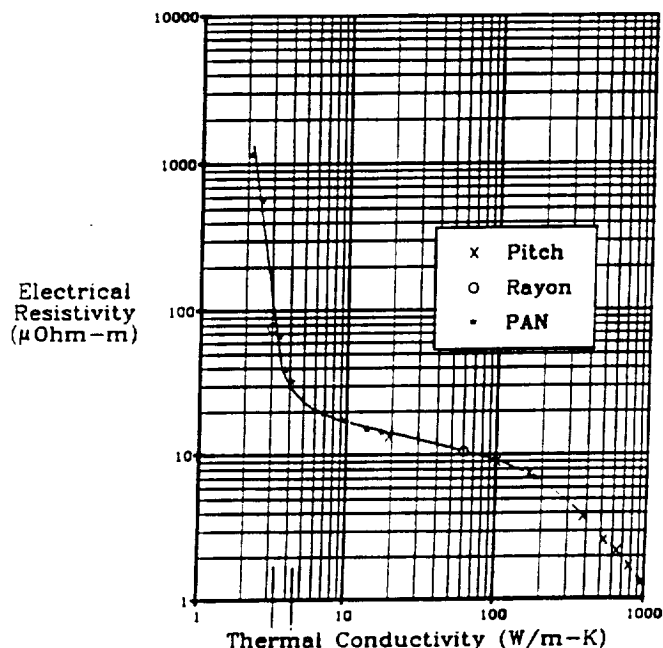


Fig. 2 Electrical Resistivity Versus Thermal Conductivity for Carbon Fiber (from M. Towne, Amoco Performance Products, Inc.)

All of the candidate low-conductivity PAN-based fibers exhibited activated-carbon characteristics similar to those of shuttle-grade rayon-based fiber. The predominant activated-carbon characteristics of concern are fiber sensitivity to moisture adsorption and the effect of adsorbed moisture on fiber electrical resistance. The effect of adsorbed moisture on electrical resistance was determined on both rayon- and PAN-based fiber: as-received, moisture-saturated, and dried. The electrical resistance of rayon-based fabric was insensitive to the amount of moisture adsorbed; however, the electrical resistance of the low-conductivity PAN fibers increased with adsorbed moisture. This finding suggested that the PAN-based fibers under study could reflect a range of electrical resistance values that was proportional to the adsorbed water content; therefore, to assess the role of moisture, electrical resistance measurements were made on unsized PAN yarn tows as-received, with no environmental conditioning, and after being dried 2 h under vacuum at 105°C.

Fiber yield and density are also affected proportionally by moisture adsorption; therefore, all three fiber properties in Eq. (1) are influenced by adsorbed moisture. Rather than prejudice the best method to apply, we determined electrical resistivity by three methods.

Method 1. Determine resistivity with specimens as-received electrical resistance, as-received yield, and vacuum-dried density.

Method 2. Determine resistivity with specimens as-received electrical resistance, vacuum-dried yield, and vacuum-dried density.

Method 3. Determine resistivity with specimens vacuum-dried electrical resistance, vacuum-dried yield, and vacuum-dried density.

Electrical resistivities determined by the three methods are summarized in Table IV. Moisture-saturated low-conductivity PAN-based fibers have substantially higher electrical resistivities than those determined by Method 1, but were not deemed pertinent to this effort. The candidate yarn most affected by moisture level was Avcarb G, which would not register a constant electrical resistance after vacuum drying. The analytical method of choice is Method 3, which gives repeatable property values. Method 2 may give more accurate results for an activated carbon fiber within a phenolic resin, since rayon-based fiber is known to retain about 1% water.⁹⁻¹⁰ This additional water is apparently trapped within the activated carbon fiber and is provided by the phenolic resin condensation reaction.¹¹

Vendor literature for rayon-based fabric (Amoco-VCL) indicates a typical fiber electrical resistivity of 59 $\mu\Omega$ -m. This value was initially presented to all of the fiber manufacturers as the major program goal—equivalent or better. In order to verify this value, electrical resistivity measurements were made at LPARL on historical samples of fabrics from Hitco, Polycarbon, and Amoco. The

warp yarn data presented in Tables IV and V suggest that the 59 $\mu\Omega\text{-m}$ value represents products CCA3/CSA and VCL manufactured 10 years ago. Recent production fabric has much lower resistivities. The resistivity of current production CCA3 and CSA fabric appears to fall in between 45 and 54 $\mu\Omega\text{-m}$. Fill-yarn resistivities were generally slightly higher, but within 2% of the warp values. Most informative were the values derived from Polycarbon, Inc., parametric fabrics processed in 1987. "Control" in this

Table IV ELECTRICAL RESISTIVITY OF PAN FIBERS

Yarn Identification	Electrical Resistivity ($\mu\Omega\text{-m}$)		
	Method 1 ¹	Method 2 ²	Method 3 ³
Avcarb G	67.700	63.250	Unstable
R879-01	326	308	282
T-350/23X AB	93.4	88.4	82.3
R879-02	84.7	80.6	75.4
Avcarb B-2	71.4	66.8	64.4
T-350/25X AB	63.9	61.4	60.6
DG Rayon 2	35.2	35.0	34.8
DG Rayon 1	27.6	27.5	26.8

¹ No consideration for adsorbed moisture

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² Cross-section area corrected for adsorbed moisture

³ Resistance and cross-section area corrected for adsorbed moisture

Table V HISTORICAL SURVEY OF RAYON-BASED FABRIC FOR ELECTRICAL RESISTIVITY

Fabric Identification	Carbonization Date	Electrical Resistivity ($\mu\Omega\text{-m}$)
Hitco CCA3		
Rec for 1983	1982	62.6
Roll 15688	1984	67.0
Roll 17909-2	1986	53.7
Roll 18954	1986	53.4
Roll 44001	1988	48.6
Roll 70023-80 (NAR)	1990	49.3
Roll 70027-65 (NAR)	1990	44.6
Roll 70036-50 (NAR)	1990	47.6
Polycarbon/NASA Parametric Study		
10B	1987	71.9
-200°F	1987	57.2
-100°F	1987	54.2
Control (CSA)	1987	46.9
+100°F	1987	46.9
+200°F	1987	44.1
Amoco		
VCL Roll 95	1984	64.7
VCL Roll 273	1986	63.7
VCX-12 Roll 736-1	1989	44.2

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series is the current production CSA fabric. Five additional fabrics were processed to temperatures below and above the firing temperature of the control to study the effect of firing temperature. For comparison, conventional T-300 and AS-4 yarns were tested; they had electrical resistivities of 17.6 and 15.8 $\mu\Omega\text{-m}$ respectively.

In summary, the thermal conductivities of six of the candidate PAN-based yarns are lower than those of conventional rayon and two are slightly higher. All eight candidate PAN yarns offer significantly lower thermal conductivity than conventional PAN-based yarn, T-300 or AS-4.

CARBON ASSAY

A LECO carbon analyzer was used to measure the carbon content of candidate PAN fibers. Prior to analysis, all samples were vacuum dried overnight at 105°C to remove adsorbed moisture. Table VI summarizes the results, which are the average of four runs for each candidate yarn, and range from a low 75.0 wt % for Avcarb G to a high of 89.0 wt % for DG rayon. The carbon contents correlate with the electrical resistivities for the candidates from each manufacturer. Specifically, Avcarb G had a higher electrical resistivity than Avcarb B-2, and the corresponding carbon contents reflect the same firing-temperature relationship. However, ranking all of the candidate yarns by carbon content does not match the ranking by electrical resistivity. This departure is attributed to (1) variations in precursor or stabilization process at the carbonization level or (2) testing accuracy or precision. Six candidate yarns were above the program goal of 80 wt % carbon minimum and two candidates were below it.

Table VI CARBON ASSAY OF PAN FIBERS

Yarn Identification	A/R Carbon Assay ¹ (wt %)
DG Rayon 1	89.0
DG Rayon 2	87.0
Avcarb B-2	84.4
T-350/25 x AB	84.2
T-350/23 x AB	83.7
R879-02	82.7
R879-01	78.9
Avcarb G	75.0
<u>Reference Data</u>	
Shuttle-Grade Rayon Fabric	96.0 min.

¹LECO carbon analyzer, four runs each

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MOISTURE ADSORPTION CAPACITY

Moisture adsorption capacity was measured as percent weight gain of moisture adsorbed by the candidate yarn when exposed to a 95–100% RH environment at 23°C for 24 hours (reference specification WS-23439 and SPIP-1). This measurement can be used to rank the candidate yarns by their carbon activated states — a very high adsorption capacity value indicates a very highly activated state.^{8,9} Table VII summarizes moisture adsorption capacities and corresponding isopropanol (IPA) adsorption capacities. The moisture adsorption capacities for all of the candidates are generally inversely related to firing temperature. Each manufacturer precursor and process, however, develops an independent relationship. Avcarb G and B-2 both have high adsorption capacities (8.92 and 7.70 wt %, respectively), while the two Hercules candidates have higher proportional variation, 6.65 versus 3.60 wt %. All of the candidate PAN yarns were well below the moisture adsorption capacity for shuttle-grade rayon-based fabric (13–16 wt %).⁸

The adsorption capacity for IPA was measured to provide Fiberite with information on prepreg processing sensitivity to SC-1008 resin solvent. Preferential adsorption of solvent by the candidate yarn could significantly influence resin pickup and uniformity. In addition, high solvent retention could increase the level of residual volatiles in the composite. The procedure for measuring the capacity for absorption of IPA was similar to the procedure for water, but with IPA replacing water vapor in the saturated atmosphere. In general, adsorption capacity values for IPA were about 60% less than for water but sufficiently high to be of concern to the prepreg operation.

FIBER DENSITY

Specific gravities were determined by the density gradient technique, ASTM-D1505 and WS-23439.^{12,13} Triplicate loops of unsized yarn were run on each candidate and all specimens were predried under vacuum at 105°C for 16 h minimum. The fiber

densities after 3-h immersion are summarized in Table VIII. These results represent the average densities measured for three yarn specimens from the run start spool and three yarn specimens from the last spool produced. The only outlier candidate yarn was Avcarb G, with a density of 1.652 g/cm³. The other seven candidates fall in a narrow range of fiber densities: from 1.759 to 1.788 g/cm³. Although the density of Avcarb G was low after 3-h immersion, gradient column fluid intrusion was progressive, and after 24-h immersion, the apparent fiber density increased to 1.687 g/cm³. The apparent density after 24 h is still significantly lower than those of the other seven candidate PAN yarns; therefore the composite density with Avcarb G fiber should be measurably lower. Composite density with the other seven candidate yarns should be similar.

Table VII ADSORPTION OF WATER AND IPA BY PAN FIBERS

Yarn Identification	Moisture Adsorption Capacity (wt %) ¹	Isopropanol Adsorption Capacity (wt %) ¹
DG Rayon 1	1.07	0.36
DG Rayon 2	1.53	0.46
R879-02	3.60	1.11
T-350/25 x AB	3.70	0.68
T-350/23 x AB	5.66	1.25
R879-01	6.65	2.42
Avcarb B-2	7.70	1.80
Avcarb G	8.92	3.96
<u>Reference Data</u>		
Shuttle-Grade Rayon Fabric	13 to 16	0.80
Conventional PAN, AS4 or T-300	0.2	~ 0.2

¹ Weight gain when exposed to 100% RH for 24 h at 23°C

0636_PPEH

Table VIII DENSITIES OF PAN FIBERS

Yarn Identification	Fiber Density ¹ (g/cm ³)
Avcarb G	1.652
Avcarb B-2	1.759
R879-01	1.771
T-350/23 x AB	1.782
DG Rayon 1	1.786
T-350/25 x AB	1.784
DG Rayon 2	1.782
R-879-02	1.788
<u>Reference</u>	
Shuttle-Grade Rayon Fabric	~1.500
AS-4 Rayon (LPARL)	1.811
T-300 (LPARL)	1.734

0636_PPEH

¹ By density gradient technique.
Ref. WS-23439 and ASTM D-1505, 3-h Value

ASH AND ALKALI METAL CONTENT

All of the alkali metals—Na, K, Ca, Mg, and Li—were determined by conventional atomic-absorption techniques (ref. specifications STW4-3184A and WS-23439). Table IX summarizes ash and alkali-metal contents for all eight candidate PAN yarns. These results are a direct reflection of precursor purity, since no attempt was made by the manufacturers to purify these candidates after carbonization. The level of K was highest in Amoco and Textron candidates, and the Na level was highest in fiber produced by BASF and Hercules. None of the low-conductivity PAN candidates had measurable amounts of Li. For potential heat-shield applications, all alkali metal contents are normally converted to Na equivalents. Table X ranks all eight candidate PAN yarns with respect to Na equivalents, applying weighting factors from specification WS-23439. Only Amoco and Textron candidate yarns are below a desirable 200-ppm maximum limit for heat-shield application.

Table IX ASH AND ALKALI METALS IN PAN FIBERS

Yarn Identification	Purity Level ¹					
	Ash (wt %)	Na (ppm)	K (ppm)	Ca (ppm)	Mg (ppm)	Li (ppm)
T-350/25 x AB	0.057	9.1	8.6	0.94	9.5	0
T-350/23 x AB	0.020	5.1	11.0	2.4	8.6	0
Avcarb B-2	0.078	40.0	94.0	3.6	9.5	0
Avcarb G	0.077	31.5	71.0	2.1	11.0	0
DG Rayon 1	0.185	207	32.0	20.0	41.0	0
DG Rayon 2	0.200	194	42.0	28.0	50.0	0
R879-01	0.347	971	7.1	4.1	15.1	0
R879-02	0.367	940	8.1	3.2	21.0	0
<u>Reference Data</u>						
Shuttle Spec.	0.50 Max.	1200.0 Max.	—	—	—	—

¹ Procedure STW4-3184

0835_PPEH

TENSILE PROPERTIES

Fiber tensile properties were measured on yarn prepregged with epoxy resin, oven cured and tested per the ASTM-D4018 procedure. Tensile strength, modulus, and strain-to-failure values are summarized in Table XI. Carbon fibers from PAN precursor are used extensively in structural composites because of their superior mechanical properties compared to rayon-based fiber. As expected, all of the candidate low-conductivity PAN yarns had tensile strengths higher than those of rayon-based fiber; however, the tensile strengths of many of the candidate yarns were significantly below the strengths of corresponding commercial yarns. Excluding Avcarb G, the seven candidate yarns had tensile strengths between 317 and 462 ksi, moduli between 21.0 and 25.3 msi, and strain-to-failure between 1.28 and 1.61%. Avcarb G yarn showed good tensile and modulus values, 190 ksi and 10.5 msi respectively, and a very good strain-to-failure, 1.77%.

The tensile properties of all eight candidate PAN yarns are all higher than conventional rayon-based yarn used in ablative composites.

Table X SODIUM EQUIVALENTS IN PAN FIBERS

Yarn Identification	Na Equivalents ¹
T-350/25 x AB	25.5
T-350/23 x AB	26.3
Avcarb G	160.7
Avcarb B-2	211.1
DG Rayon 2	272.0
DG Rayon 1	273.0
R879-02	956.9
R879-01	986.2

¹ Alkali metal weighting factors
(WS-23439):

Na	1	Ca	0.4	Li	3.0
K	1.8	Mg	0.05		

0636_PPEH

Table XI TENSILE PROPERTIES OF PAN FIBERS

Yarn Identification	Tensile Strength ¹ (psi)	Tensile Modulus ¹ (Msi)	Strain-To-Failure ¹ (%)
R879-01	339,000	21.0	1.53
R879-02	411,000	24.9	1.57
Avcarb B-2	317,000	21.1	1.48
Avcarb G	190,000	10.5	1.77
T-350/25 x AB	320,000	24.2	1.28
T-350/23 x AB	348,000	22.8	1.44
DG Rayon 1	462,000	25.3	1.54
DG Rayon 2	454,000	23.8	1.61
<u>Reference Data</u>			
Shuttle-Grade Rayon Fabric	50 to 100,000	8 TO 9	0.6 to 1.1
T-300 PAN	530,000	33.5	1.58
AS4 PAN	590,000	36.0	1.65

¹ ASTM-D4018

0636_PPEH

OXIDATION RATE

The sensitivity of carbon fiber to air oxidation/gasification may not be a significant discriminating fiber characteristic for nozzle applications, since most solid rocket motor exhaust gas is a reducing atmosphere.⁸ This program, however, is also tasked to investigate low-conductivity PAN fiber potential for heat-shield application, which will subject the carbon fiber to air oxidation. The test method used to assess the eight candidate PAN-based yarns was presented in a previous JANNAF/RNTS paper which correlated the oxidation resistance of rayon-based fiber with firing temperature and sodium content.¹⁴ Briefly, the test procedure uses a Perkin Elmer TGA apparatus to measure low-temperature (zone 1) oxidation mass loss rates at isothermal temperatures near

500°C. These rates are plotted versus $1/T$ values to develop classical Arrhenius plots. The Arrhenius equation form is presented in Eq. (2).

$$k = A e^{-E_a/RT}$$

where

- k = specific reaction rate, s^{-1}
- A = pre-exponential factor, s^{-1}
- E_a = activation energy, cal/mole carbon
- R = gas constant, cal/mole-K
- T = absolute temperature, K

Arrhenius plots for the four manufacturers are presented in Fig. 3. All candidates from Amoco, Hercules, and BASF compare favorably to conventional shuttle-grade rayon-based fiber. The two candidate yarns from Textron Specialty Products, however, show distinctly different behavior; in particular, fiber oxidation rates at temperatures below 550°C are progressively higher for both Textron candidates, Avcarb B-2 and G. The relatively low alkali metal content of these products suggests that this variation in behavior must be unique to the PAN precursor used and/or due to a different stabilization processing technique used by Textron. The Textron-product Arrhenius plots, however, all showed good compliance to the Arrhenius equation. The Arrhenius plots were subsequently

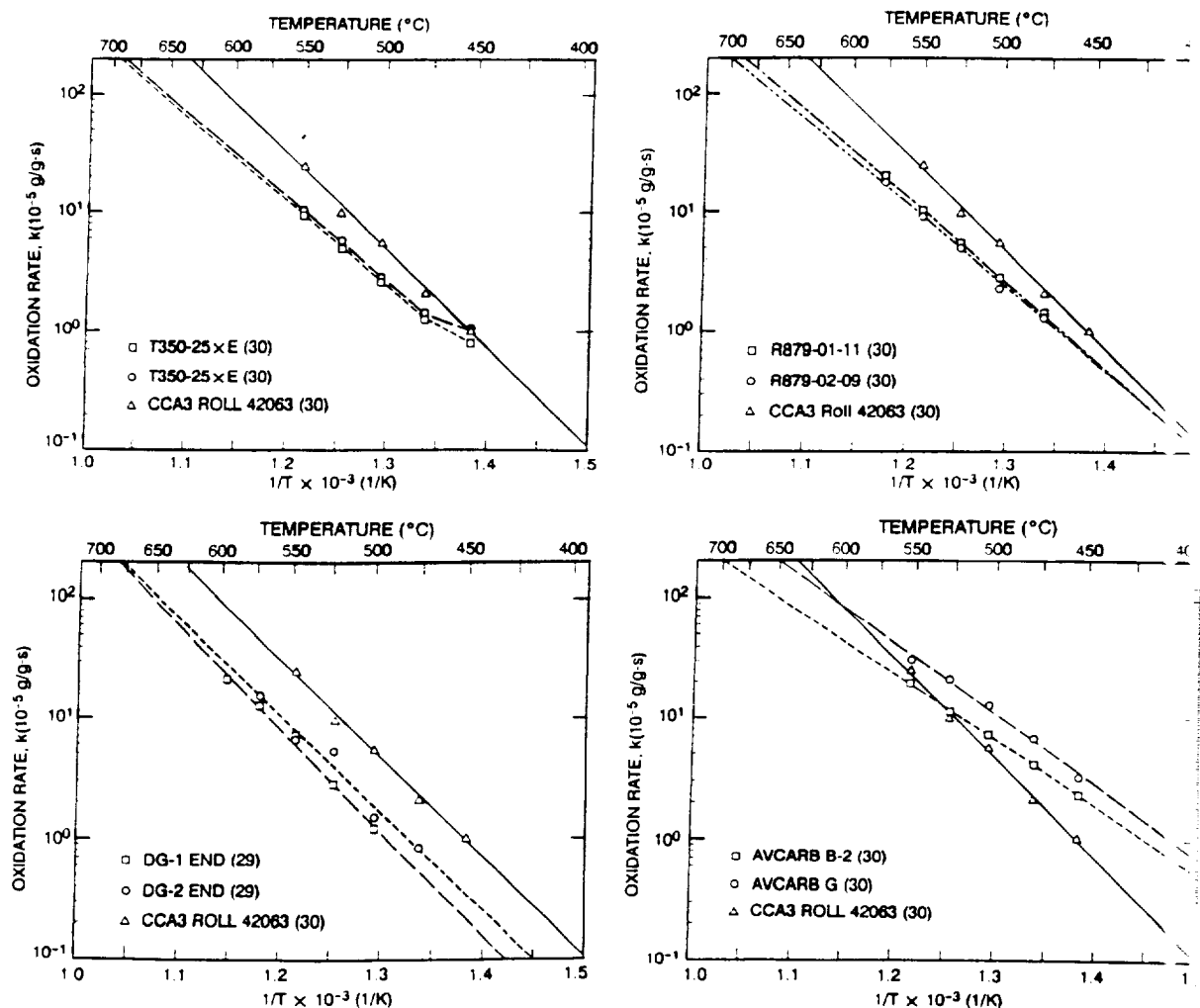


Fig. 3 Arrhenius Plots for PAN-Based Fiber

used to calculate a reaction activation energy and pre-exponential values, presented in Table XII. The unique behavior of the Textron yarns is reflected in significantly lower E_a and A values.

Table XII ARRHENIUS EQUATION CONSTANTS FOR PAN FIBERS

Yarn Identification	Air Oxidation Mass Loss ¹ Arrhenius Equation Values	
	Activation Energy (E_a , K cal/mol)	Pre-Exponential (A , g/gs)
R879-01	33.0 ± 0.9	6.02 x 10 ⁴
R879-02	32.0 ± 1.8	2.91 x 10 ⁴
Avcarb B-2 (end)	26.6 ± 0.3	2.33 x 10 ³
Avcarb G (end)	26.8 ± 1.4	4.30 x 10 ³
T-350/25 x AB (end)	32.6 ± 0.8	4.29 x 10 ⁴
T-350/23 x AB (end)	32.7 ± 1.6	5.00 x 10 ⁴
DG Rayon 1 (end)	39.2 ± 2.4	1.56 x 10 ⁶
DG Rayon 2 (end)	36.9 ± 3.5	4.90 x 10 ⁵
<u>Reference Data</u>		
Shuttle-Grade Rayon Fabric	37.4 ± 1.7	1.91 x 10 ⁶

¹ Reference 14

0636_PPEH

HIGH-TEMPERATURE EFFECTS

The ablation char zone will be exposed to temperatures far in excess of the fiber firing temperatures used for all of the candidate PAN-based yarns; therefore, serious consideration was given to the effect of high temperature on fiber properties. For structural applications, a major attribute of PAN-based fiber is a pronounced sensitivity to high-temperature heat treatment (HTHT). HTHT is known to produce preferred lattice structure orientation in PAN-based fiber and to increase fiber modulus, thermal conductivity, and density. Skeins of candidate yarn were batch processed at LPARL up to 2500°C (4532°F) in an argon atmosphere to assess the HTHT effects. The thermal cycle required 6 h to reach 2500°C, and the sample was held at 2500°C for 5 min prior to cooldown. Table XIII summarizes the effect of HTHT on yield, nominal filament diameter, weight loss, carbon yield, length change, density, and electrical resistivity. For comparison, Table XIII also includes as-received carbon content, yield, and nominal filament diameter. The as-received carbon contents are generally higher than HTHT carbon yields. The variance is much larger for the candidate yarns with lower carbon contents submitted by each of the manufacturers. This suggests that the oxygen content of these eight candidate products is responding to different precursor processing and firing temperatures. During HTHT, chemisorbed oxygen will

Table XIII EFFECTS OF HIGH-TEMPERATURE HEAT TREATMENT ON PAN FIBERS

Yarn Identification	As Received			2500°C (4532°F) Heat Treatment ¹						
	Carbon Assay (wt %)	Yield ² (g/cm ³) x 10 ⁻³	Nominal Diameter ³ (μm)	Yield ² (g/cm ³) x 10 ⁻³	Nominal Diameter ³ (μm)	Weight Loss (%)	Carbon Yield (wt %)	Linear Change (%)	Density (g/cm ³)	Resistivity (μΩ-m)
R879-01 (03)	78.9	2.29	7.4	1.81	6.3	22.3	77.7	-1.47	1.917	8.40
R879-02 (04)	82.7	2.21	7.3	1.75	6.2	21.3	78.7	-0.80	1.917	8.29
Avcarb B-2	84.4	2.46	7.7	2.01	6.8	18.5	81.5	+0.44	1.838	9.19
Avcarb G	75.0	2.84	8.5	2.04	6.9	28.2	71.8	-1.80	1.842	9.11
T-350/25 x AB	83.6	2.32	7.4	2.00	6.7	15.7	84.3	-0.84	1.931	8.56
T-350/23 x AB	83.7	2.36	7.5	1.99	6.6	16.3	83.7	-0.88	1.928	8.68
DG Rayon 1	89.0	1.90	6.7	1.68	6.1	12.2	87.8	-0.50	1.926	8.50
DG Rayon 2	87.0	1.96	6.8	1.64	6.0	15.5	84.5	-0.59	1.918	8.51

¹ Procedure SPIP-2

² Vacuum dried at 105°C for 16 h

³ Based on 3000 filaments per tow

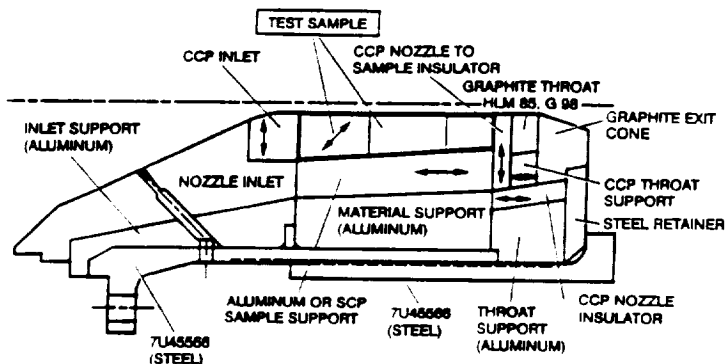
0636_TWSTBL

leave the surface with a carbon atom at a ratio of 1:1 or 1:2 (CO or CO₂). Carbon atoms leaving the surface as oxides will lower the carbon yield derived from the HTHT study, but all carbon atoms will be measured in the as-received carbon assay test.

Table XIII also summarizes nominal filament diameter before and after HTHT. For this analysis, we assumed all candidate yarns contained 3,000 filaments. The Tektron products exhibited the largest as-received filament diameters and conversely the largest nominal filament diameters after HTHT. The Textron yarn Avcarb B-2 was also the only candidate PAN-based fiber that grew in length (0.44%) during HTHT.

SUBSCALE TEST EVALUATION

The eight candidate low-conductivity PAN-based products were evaluated for motor performance (erosion, char, structural integrity) using Thiokol Corporation's 40-lb propellant cartridge subscale test motor (FPC). The test motor, shown in Fig. 4, consists of a blast-tube-material-test section, a bulk graphite throat, and surrounding carbon phenolic insulation. The test-section materials were at a contraction ratio of 1.26:1. The motor operates at 600 to 700 psi pressure for approximately 30 s, using 88/20 HTPB propellant. The test section was configured to provide heat flux and heat transfer coefficients similar to a conventional solid rocket motor. Initial plans are to evaluate all candidate products. One material, Hercules R879-02 (LF PAN 2), has been tested; the remaining materials are planned for testing in early October.



- HEAT FLUX AND HEAT TRANSFER COEFFICIENT ARE SIMILAR TO SRM INLET (SIMILAR EROSION RATES)
- OPERATING PARAMETERS
 - PROPELLANT - HTPB DLH-428 88/20
 - $P_c = 600-700$ psia
 - $t_b = 30$ s
 - THROAT DIAMETER 0.446 in.
 - BLAST TUBE DIAMETER 0.50 in., $\epsilon = 1.26$

Fig. 4 Thiokol Corp. 40-lb-Charge Subscale Test Motor

Hercules R879-02 yarn-based panels were tested with 45° and 90° to centerline ply angle sections. The 45° ply angle section simulates a typical nozzle component with respect to erosion and char. The 90° section is used for fiber thermal structural evaluation, since this orientation maximizes fiber tensile stress. Tag end properties were taken on both parts. Resin content was high (40%), and edgewise compressive strength was also on the high side (41,685 psi); properties are listed in Table XIV.

Table XIV Hercules R879-02 Panel Properties

Density	1.574 g/cm ³
Volatiles	1.00%
Resin	40.18%
Barcol Hardness	59.83
Edgewise Compression	41,685 psi

Erosion and char data are presented in Fig. 5. Erosion in the 45° section varied between 6.7 to 8.0 mils/s, erosion in the 90° section was higher, at 7.4 to 11.2 mils/s. This is 11% and 38% higher than FM5014-graphite cloth phenolic tested in the same environment. The low-fired PAN charred slightly less than FM5014 (0.33 in. versus 0.37 in.).

Figure 6 shows the postfired nozzle cross section. The 45° section indicates good integrity, uniform char, and no delaminations; the 90° section, however, did not perform as well. Spallation occurred at the aft section and fiber tensile failure was present the full length of the 90° section at the char-virgin interface. This spallation and fiber failure is not typical of standard heat-treated PAN materials.

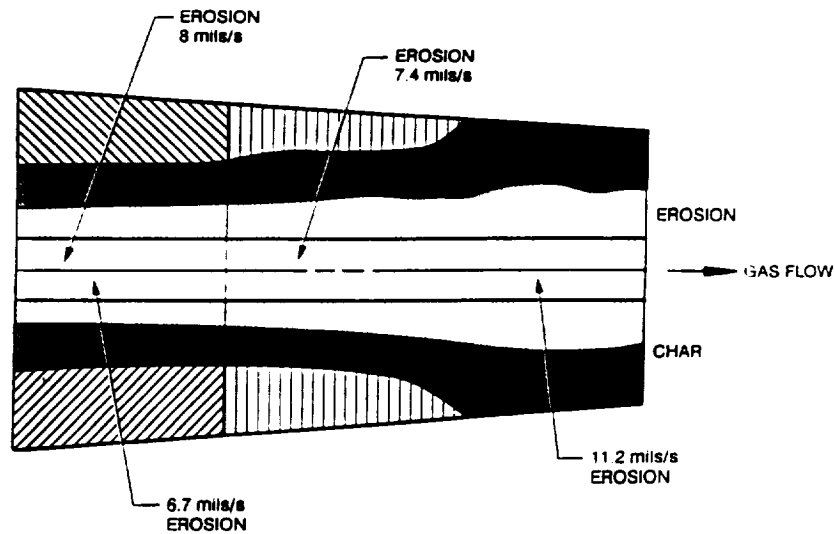


Fig. 5 Hercules R879-02 Fiber Erosion Profile

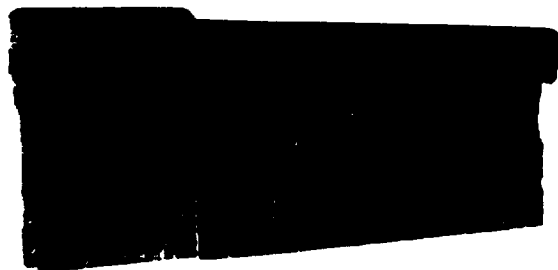


Fig. 6 Postfiring Cross-Section View of Hercules R879-02 Yarn (LF PAN 2)

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APPENDIX D

JACK WILLIAMSON

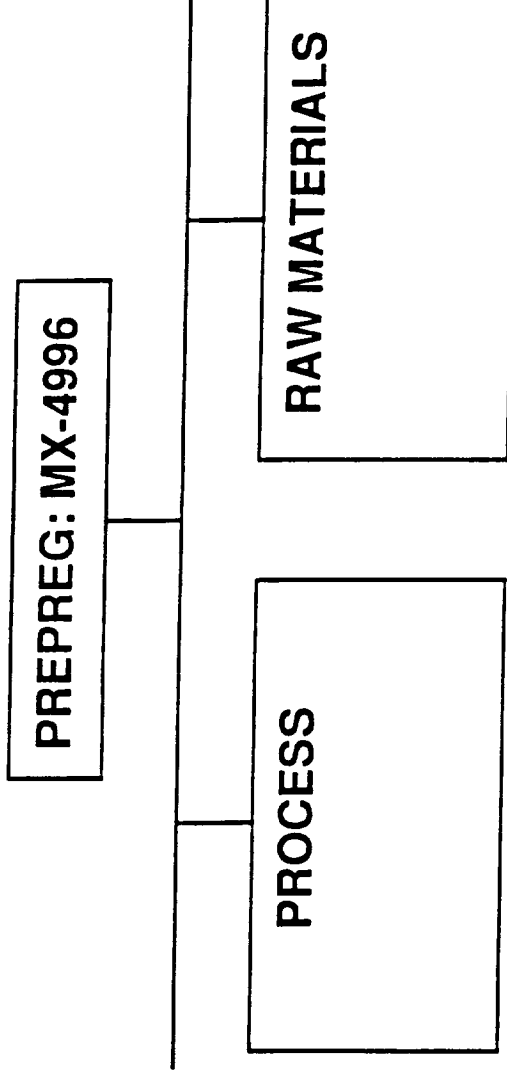
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Prepreg Evaluation (a first cut)

ORIGINAL PAGE 11
OF POOR QUALITY

Presented by: J. B. Williamson

PREPREG: MX-4996



PREPREG: MX-4996

MANUFACTURING PROCESS

- SOLUTION IMPREGNATION
- HOT AIR OVEN DESOLVATION
- HOT AIR OVEN "B" STAGING
- SINGLE CONTINUOUS OPERATION

PREPREG: MX-4996

MANUFACTURING PROCESS

- **PRODUCT FORMS**
 - **FULL WIDTH FABRIC ROLL**
 - **SLIT TO WIDTH CONTINUOUS WARP TAPE**
 - **SHEARED TO WIDTH $\pm 45^\circ$ SEWN STRIP BIAS TAPE**
 - **POTENTIAL MOLDING COMPOUND: CHOPPED 1/2"x1/2" PREPREG FABRIC**

PREPREG: MX-4996

RAW MATERIALS

- **FABRIC: POST-WOVEN CARBON YARN**
- **PRECURSOR: RAYON 1 PLY 1650 DERNIER YARN**
- **SUPPLIED BY NORTH AMERICAN RAYON TO POLYCARBON IN VALENCIA, CALIFORNIA**
- **POLYCARBON PLYS 5 SINGLE-END 1650 DERNIER YARNS INTO SINGLE 5-PLY YARN FOR CONVERSION INTO CARBON**
- **RAYON SOLE SOURCE: NORTH AMERICAN RAYON**

**NOTE: RAYON NOT DISCUSSED - TO BE TREATED IN
DETAIL BY NORTH AMERICAN RAYON**

PREPREG: MX-4996

RAW MATERIALS

- POLYCARBON: INDIVIDUAL YARN CARBONIZATION
- STARTING STOCK: 5 PLY 1650 DERNIER RAYON
- TWO-STAGE PROCESS
 - LOW TEMPERATURE LONG-TIME (1MONTH) PRE-OX
 - HIGH TEMPERATURE SHORT-TIME FINAL PROCESS (TBD)
- ** FIBERITE PROPRIETARY SURFACE FINISH APPLIED
- PRODUCT FORM AVAILABLE: 1/4 TO 5LB WOUND ON 3" CORE
- SPECIAL PACKAGING AVAILABLE ON REQUEST

**** AVAILABLE FROM FIBERITE BY SPECIAL ARRANGEMENT**

PREPREG: MX-4996

RAW MATERIALS

- RESIN: PHENOLIC
- SC1008 MANUFACTURED BY BORDEN CHEMICAL
- FORM: ALCOHOL VARNISH AVAILABLE IN
 - DRUM LOTS
 - TANK TRUCK
 - TANK CAR
- STORAGE: REFRIGERATION REQUIRED
- SC1008 IS NON-PROPRIETARY AND IN GENERAL USE BY THE ABLATIVE COMMUNITY

PREPREG: MX-4996

RAW MATERIALS

- FILLER: HIGH PURITY CARBON **
 - MICRON SIZE PARTICLES
 - MEDIUM FURNACE BLACK
 - CANADIAN PETROLEUM INDUSTRY SOURCE

**** NOT THE SAME FILLER AS USED IN MX-4926**

PRE-PREG FM-5939 *



PROCESS

RAW MATERIALS

* OLD DESIGNATION FM-5055 IMPROVED

PREPREG FM-5939 (OLD DESCRIPTION FM-5055-IMPROVED)

MANUFACTURING PROCESS

SOLUTION IMPREGNATION

HOT AIR OVEN DESOLVATION

HOT AIR OVEN "B" STAGING

SINGLE CONTINUOUS OPERATION

B2JBW

PREPREG FM-5939 (OLD DESIGNATION FM-5055 IMPROVED)

MANUFACTURING PROCESS

PRODUCT FORMS

FULL WIDTH FABRIC ROLL

SLIT TO WIDTH CONTINUOUS WARP TAPE

SHEARED TO WIDTH $\pm 45^{\circ}$ SEWN STRIP BIAS TAPE

POTENTIAL MOLDING COMPOUND

CHOPPED 1/2" X 1/2" PREPREG FABRIC

B3JBW

PREPREG FM-5939

RAW MATERIALS PRE-WOVEN RAYON FABRIC

RAYON YARN SUPPLIER NORTH AMERICAN RAYON CORPORATION
MATERIAL FORM SINGLE PLY SOLE SOURCE

FABRIC SUPPLIER HIGHLAND INDUSTRIES
ALTERNATE MILLIKEN

FABRIC CONSTRUCTION

8 HARNESS SATIN SINGLE PLY 1650 DENIER
LOOM HIGH SPEED DRAPER

B4JBW

PREPREG FM-5939

RAW MATERIALS PRE-WOVEN CARBON FABRIC
CARBONIZER

BP CHEMICALS ADVANCED MATERIALS DIVISION
PROCESS

TWO STAGE

PRE-OX LONG TIME LOW TEMPERATURE (1 MONTH)

FINAL CONVERSION SHORT TIME HIGH TEMPERATURE

EXACT CYCLE T.B.D. BY VENDOR

B5JBW

PREPREG FM-5939

RAW MATERIALS

PHENOLIC RESIN 91LD

SUPPLIER

STUART IRONSIDES CORP.

FORM

ALCOHOL VARNISH DRUM LOTS
TANK TRUCK TRANK CAR.

STORAGE

REFRIGERATION REQUIRED

91LD

PROPRIETARY SOLE SOURCE
AVAILABLE FROM BP CHEMICALS
BY SPECIAL ARRANGEMENT

B6JBW

PREPREG FM 5939

RAW MATERIALS

FILLER

USP # 28

MEDIUM FURNACE BLACK

MICRON SIZE PARTICLE

PETROLEUM SOURCE

FORIEGN SOURCE CANADIAN

APPENDIX E

MYLES TOWNE

**FABRIC OXIDATION
MASS LOSS TEST**

COMPARISON: Sample in Petri Dish vs. Weighing Bottles

Petri dish - 20mm x 100mm

Tall Weighing Bottle - 40mm ID x 80mm high Approx. 75

Low Weighing Bottle - 70mm ID x 33mm high Approx. 107

Furnace Temp: 382°C

Samples: 1.5 - 2.0 grams

	N. Hollywood		VCL (NARS)	
	<u>4-3/4 hr</u>	<u>19-3/4 hr</u>	<u>4-3/4 hr</u>	<u>19-3/4 hr</u>
Petri Dish	39.99	100	3.81	11
	31.19	100	3.26	13
	<u>23.13</u>	<u>100</u>	<u>3.56</u>	<u>14</u>
ave.	31.43		3.54	14
c.v.	27%		7.8%	6
Tall Bottle	37.17	98.93	4.60	1
	34.94	98.90 white	4.08	1
	<u>39.07</u>	<u>98.94 ash</u>	<u>3.82</u>	<u>1</u>
ave.	37.06		4.17	1
c.v.	5.6%		9.5%	4
Low Bottle	47.24	91.11	4.89	:
	51.13	white	4.33	1
	<u>40.69</u>	<u>99.08 ash</u>	<u>4.99</u>	<u>1</u>
ave.	46.35		4.73	1
c.v.	11.4%		7.5%	

FABRIC OXIDATION MASS LOSS TEST

COMPARISON: SUSPENDED SPECIMEN VS. PETRI DISH

TEST OVEN: 375°C. RAPIDLY CIRCULATING AIR
FABRIC SAMPLES: ABOUT 1 GRAM SUSPENDED ON PAPER CLIPS
OR PLACED IN 100 MM X 20 MM PETRI DISHES

MATERIAL	SUSPENDED % WT. LOSS		PETRI DISH % WT. LOSS	
	<u>4 HR</u>	<u>21 HR</u>	<u>4 HR</u>	<u>21 HR</u>
VCL (NARC)	2.62	15.57	2.58	14.07
	3.45	18.12	2.82	14.70
	<u>3.16</u>	<u>16.80</u>	<u>2.82</u>	<u>15.38</u>
	AVG. 3.08	16.83	2.74	14.72
CV	13.6%	7.58%	5.06%	4.45%
N. HOLLYWOOD (1983)	29.16	100	25.01	100
	29.26	100	25.59	100
	<u>32.87</u>	100	<u>27.50</u>	100
	AVG. 30.43		26.03	
CV	6.95%		5.01%	

NOTE: SAMPLES WERE DRIED FOR 20 MIN. AT ~ 300-325°C.

APPENDIX F

ED MILLS

CARBON PHENOLIC SHELF LIFE

EDWARD MILLS

UT/CSD MATERIALS

NOVEMBER 15, 1990

CARBON PHENOLIC SHELF LIFE STANDARDIZATION

- ★ **EMPHASIS ON FM5055/MX4926 TYPE CARBON PHENOLICS USING VCL/CCA/CSA WITH MIL-R-9299**
- ★ **CARBON MATERIALS TYPICALLY MORE CRITICAL DUE TO MOISTURE EFFECTS**
- ★ **GRAPHITE & SILICA PHENOLICS SIMILAR BUT LESS SENSITIVE TO MOISTURE**

CURRENT INDUSTRY VARIATIONS MX4926/FM5055

★ STORAGE CONDITIONS

70°F MAX - 50°F MAX - 40°F MAX - 0°F MAX
MOST COMMON RARE

★ LIVES @ 50°F MAX

6 MONTHS - RETEST REQ'D AFTER 60 DAYS FROM ACCEPTANCE
6 MONTHS - WITH 3 MONTH EXTENSION (9 MONTHS MAX)
6 MONTHS - WITH 3 X 6 MONTH EXTENSIONS (24 MONTHS MAX)

★ RETEST REQUIREMENTS FOR EXTENSION

FLOW/VOLS ONLY

TO

FLOW/VOLS/RESIN CONTENT/IRPI/TACK
+ PANEL PHYSICALS INCLUDING INTERLAMINAR SHEAR

**BASIC DESIRE TO ALLOW MAXIMUM USABLE LIFE
WITH MINIMUM CONSTRAINTS CONSISTENT WITH
GOOD HARDWARE**

**PROBLEMS WITH EXTENDED LIFE MATERIALS - MATERIAL WHICH PASSES
RETEST MAY NOT MAKE "GOOD" PARTS**

- ★ **UNABLE TO WRAP/LACK OF "TACK"**
- ★ **FAILURE TO "KNIT" ON LAMINATION**
- ★ **LOW DENSITY INDICATIONS IN X-RAY OF FINAL PART**
- ★ **REDUCED INTERLAMINAR SHEAR PROPERTIES**

QUESTIONNAIRE TO INDUSTRY USERS & PREPREGGERS

★ EXPERIENCE

★ DATA BASE

★ RECOMMENDATIONS

- ✓ INITIAL ACCEPTANCE TESTS/REQUIREMENTS**
- ✓ STORAGE CONDITIONS (TEMPERATURE & HUMIDITY)**
- ✓ SHELF LIFE & EXTENSIONS PERIODS**
- ✓ RETEST REQUIREMENTS**
- ✓ OUT TIME LIMITS (TIME AND TEMPERATURE)**

ADDITIONAL COMMENTS FROM AUDIENCE

- ★ OUT TIME LIMITS (LOG)**
- ★ MOISTURE PROTECTION (SEALED W/DESSICANT VS. INERT ATMOS.)**
- ★ LOWER (0°F) STORAGE TEMPERATURE**
- ★ VARIATIONS**
 - **BIAS VS. STRAIGHT VS. BROADGOODS**
 - **TAPE WRAP PARAMETERS**
 - ✓ **DIAMETER**
 - ✓ **ANGLE TO**
 - ✓ **THICKNESS**
- **FABRICATOR'S PREFERENCES RELATIVE TO "STIFFNESS" OF PREPREG**
- ★ CONSIDER "LEVELS" OF STORAGE REQUIREMENTS AS A FUNCTION OF ABOVE USES**



SPIP NOZZLE - PHENOLIC TESTING TITAN 4 NARC RAYON QUALIFICATION

EDWARD MILLS
UNITED TECHNOLOGIES
CHEMICAL SYSTEMS DIVISION

11-15-90

PRESENTED TO

SPIP - NOZZLE INITIATIVE ADVISORY COMMITTEE
ON STANDARDIZATION OF CARBON PHENOLIC CONSTITUENT
TEST METHODOLOGY

NORTH AMERICAN RAYON
ELIZABETHTON, TN.



CSD TITAN 4

NARC RAYON QUALIFICATION

**THROAT DESIGN USES MULTIPLE THROAT RINGS FABRICATED BY
FLATWISE INVOLUTE LAYOUT USING FM5014 GRAPHITE PHENOLIC**

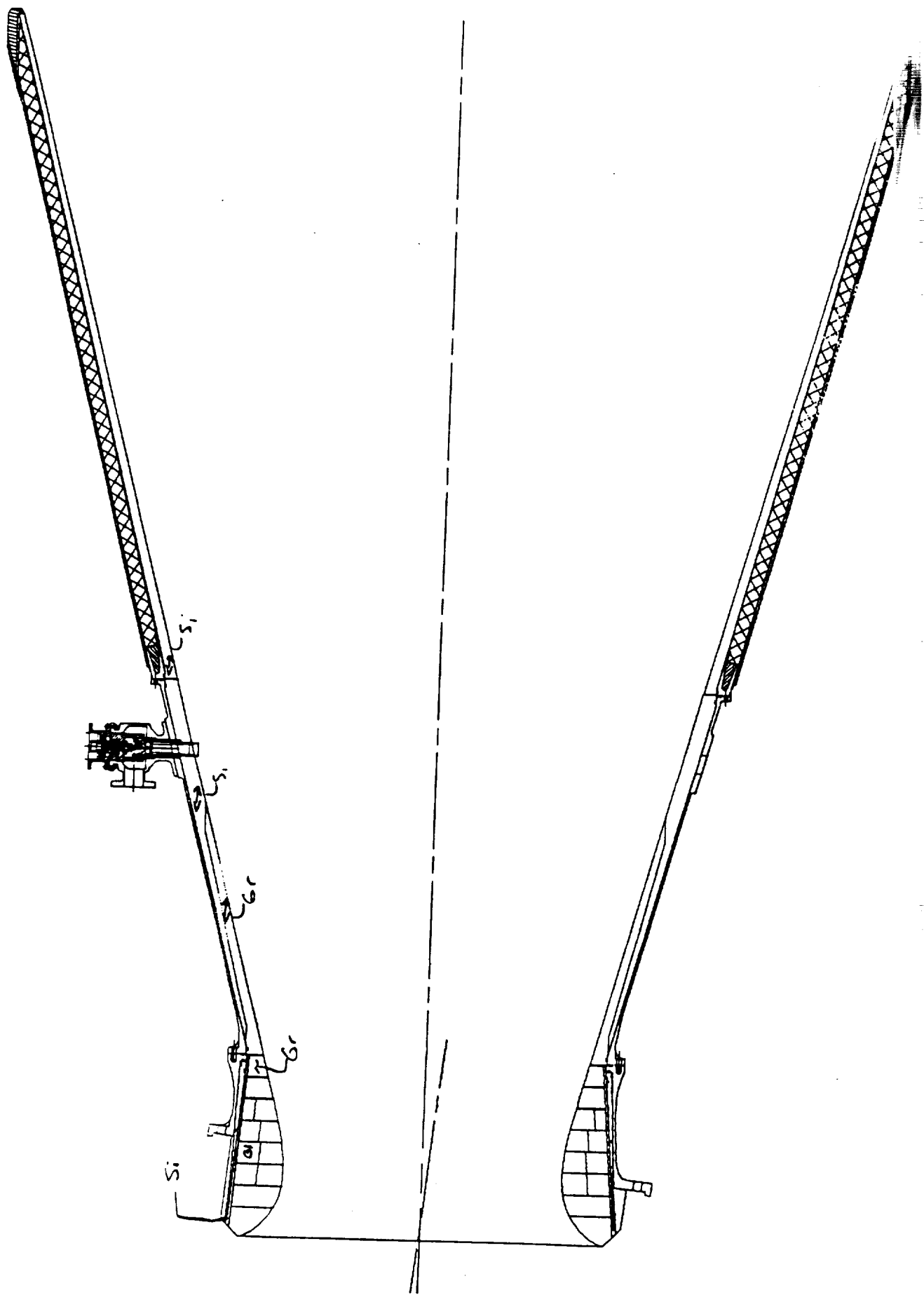
**LEADING EDGE USES CONTOUR TAPE WRAPPED MX4926/VCK CARBON
PHENOLIC**

**FORWARD EXIT CONE USES PARALLEL TO CENTERLINE TAPE WRAPPED
FM5014 GRAPHITE PHENOLIC**

ALL ABOVE USE 1100 DENIER RAYON BASED PREPREGS

**BASIC DESIGN FIRST FIRED DECEMBER 1964 - IRC RAYON
QUALIFIED AND CHANGED TO AVTEX RAYON - 1978**

T4NARC1



CSD TITAN 4

NARC RAYON QUALIFICATION

MX4926/VCK CARBON PHENOLIC PER CSD SPECIFICATION SE0116

MIL-R-9299 RESIN (SC1008)

CARBON CLOTH PER SE0091 (AMOCO VCK - INTERMEDIATE FIRED)

RAYON CLOTH - AMOCO SPECIFICATION RM2285

GRADE 435 = 5 HARNESS SATIN, 2 PLY, NARC RAYON
1100 DENIER, 490 FILAMENT (HIGHLAND WEAVE)

T4NARC2

CSD TITAN 4

NARC RAYON QUALIFICATION

FM5014 GRAPHITE PHENOLIC PER 4MDS-40721

MIL-R-9299 RESIN (91LD); P28 FILLER

GRAPHITE CLOTH PER 4MDS-40752 (AMOCO WCA - HIGH FIRED)

RAYON CLOTH - AMOCO SPECIFICATION RM2284

GRADE 430 = PLAIN WEAVE, 3 PLY, NARC RAYON
1100 DENIER, 490 FILAMENT (HIGHLAND WEAVE)

GRADE 420 = PLAIN WEAVE, 3 PLY, AVTEX RAYON
1100 DENIER, 490 FILAMENT (HIGHLAND WEAVE)

CSD TITAN 4

NARC RAYON QUALIFICATION

FIRING TEMP	"WCA" - 1100 DENIER ABOVE 2500°C	"VCK" - 1100 DENIER APPROX 1500°C
AMOCO SPECIFICATION RAYON CLOTH PROPS:	RM2284A (GR 430) 3 PLY, PLAIN WEAVE	RM2285A (GR 435) 2-PLY, 5-HS
WEIGHT - OZ / SQ YD	17.5 / 19.25	16.5 / 17.5
ENDS PER INCH (W)	20 / 22	28 / 30
PICKS PER INCH (F)	17 / 19	27 / 29
GAUGE - INCHES	0.033 / 0.039	0.030 / 0.035
WARP CRIMP - %	9.5 / 13.5	3.0 / 8.0
FILL CRIMP - %	2.0 / 5.0	3.0 / 8.0
WARP STRENGTH - LB	475 MIN	450 MIN
FILL STRENGTH - LB	450 MIN	450 MIN
PLIED YARN TWIST TPI	1.5 / 2.3 S	1.5 / 2.3 S

T4NARC4A

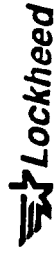
CSD TITAN 4

NARC RAYON QUALIFICATION

RAYON YARN PROPS:	1100 DENIER/490 FIL	1650 DENIER/720 FIL
	RM2284A (GR 430)	STW4-3832 (PRELIM)
	= RM2284 (10-31-77)	
COND BREAK STRENGTH	7.0 / 9.6 LB	10.3 / 13.5 LB
COND ELONGATION	5.4 / 9.4 %	5.5 / 9.5 %
DENIER	1060 / 1140	1590 / 1710
TWIST SINGLES	1.4 / 2.2 TPI - Z	1.6 / 2.4 TPI - Z
FINISH	0.2 / 1.0 %	0.2 / 1.0 %
WET SHRINKAGE	2.6 / 4.6 %	2.9 / 4.7 %
pH	5.0 / 8.0	5.0 / 8.0
MOISTURE	13.0 % MAX	13.0 % MAX
ASH	0.7 % MAX	0.45 % MAX
SULFUR	0.25 % MAX	0.25 % MAX
ZINC	0.07 % MAX	0.07 % MAX



RAYON BASED FABRIC - FIBER PROPERTIES



<u>Fiber Property</u>	<u>Low Fired</u>	<u>Intermediate Fired</u>	<u>High Fired</u>
Fiber Density, g/cc	1.46-1.53	1.46-1.50	1.44-1.45
Tensile Strength, Ksi	~100	~100	~100
Tensile Modulus, Msi	~6	~6	~6
Carbon Assay, w%	96+	99+	99.9
Ash Content, w%	0.4	0.3	0.01
Na, ppm	<600	<500	<10
Thermal Conductivity, w/mk	3.7	4.0	4.1
Surface Area, m ² /g	476-923	7	1
Surface Oxygen, atomic %	5.5 to 27	1.8 - 7.9	<1
Volume of Trapped Gasses, cc/gm	19-30	8	0.26
Moisture Adsorption Capacity, w% ¹	8-16	1-8	0.1
CO ₂ Adsorption Capacity @ 23°C, w%	17-30	0.2	0

1. Exposed to 100% R.H. @ 23°C for 24 to 25 hours

CSD TITAN 4

NARC RAYON QUALIFICATION

1. PREPREG CHARACTERIZATION

NARC vs SPECIFICATION & DATABASE

NARC PANELS 3 HT "LOTS" EACH MATERIAL

2. FABRICATE SUBSCALE TM3 PARTS & STATIC TEST

INSTRUMENTED NOZZLES

NARC vs AVTEX vs HISTORY

COPROCESSED AVTEX & NARC PANELS

3. FABRICATE FULLSCALE COMPONENTS

STANDARD NDE & TAG END ACCEPTANCE TESTS

COPROCESSED NARC PANELS FOR FULL CHARACTERIZATION

TAG ENDS FOR IN-SITU CHARACTERIZATION

Figure 4. TM-3A "Long Duration" Nozzle/Aft Closure Assembly

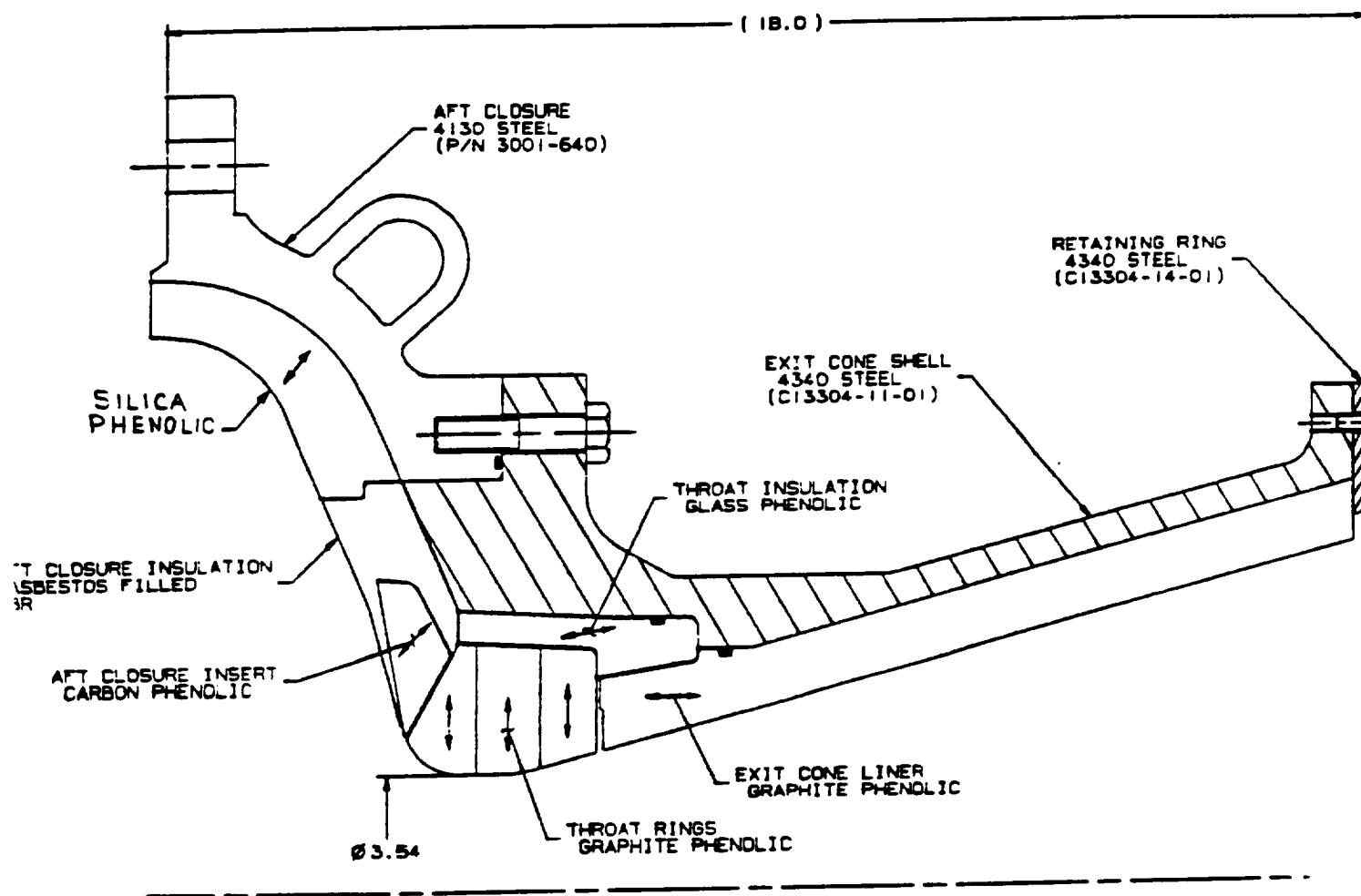
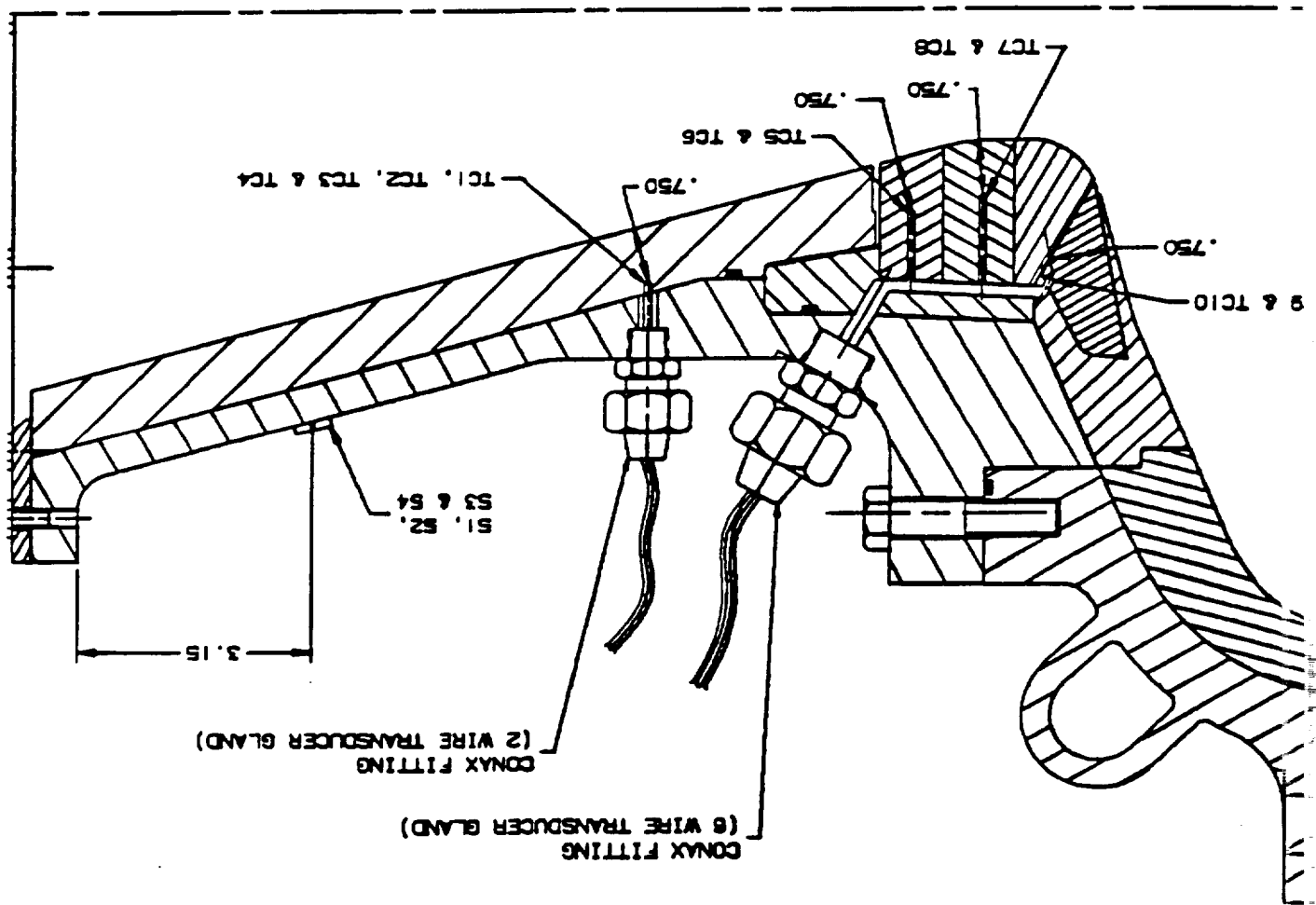


Figure 5. TM-3A "Long Duration" Nozzle Instrumentation Requirements



BAUGE	NO.	ANGULAR
S 1	0°	
S 2	90°	
S 3	180°	
S 4	270°	
TC 1	0°	
TC 2	90°	
TC 3	180°	
TC 4	270°	
TC 5	0°	
TC 6	90°	
TC 7	0°	
TC 8	90°	
TC 9	0°	
TC 10	90°	

CSD TITAN 4

NARC RAYON QUALIFICATION

- 4. THERMAL CHARACTERIZATION (AEROTHERM)**
 - HIGH TEMPERATURE, HIGH RATE, CHARRING INPUT**
 - COMPARISON TO HISTORICAL DATA SAME MATERIALS**
 - DIRECT INPUT TO ANALYSIS**
- 5. MECHANICAL CHARACTERIZATION**
 - FULL MATRIX TO 5000°F (SIMILAR TO NASA LEVEL II)**
 - ABBREVIATED MATRICES (TO 1200°F)**
 - MULTIPLE LOTS**
 - MULTIPLE PROCESSES**
 - WITH AND WITHOUT POSTCURE**
 - FULL SCALE TAG ENDS**
- 6. DETAILED THERMAL AND STRESS ANALYSIS**

T4NARC8

TABLE I

Phase I Preliminary Thermal Properties Samples

TM-3 Material	NAR	AVTEX	Panels AVTEX	NAR	Graphite Phenolic:				
					TGA	Density	Conductivity (70-300°F)	90 Wrap	45 Wrap
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1
	1	1	1	1	1	1	1	1	1

Carbon Phenolic:

TGA
Density
Conductivity
(70-300°F)
90 Wrap
45 Wrap

Phase II Full Thermal Characterization

(Samples from full scale components - tag ends)

Decomposition Kinetics
Elemental Composition
Enthalpies of Formation
Specific Heat

Conductivity (low temperature range)
Conductivity (high temperature, high flux,
dynamically measured during charring process)

k = Thermal Conductivity

TGA = Thermogravimetric Analysis

TIIPHEN4.WQ1

TABLE 1

CSD TITAN 4 - CARBON OR GRAPHITE PHENOLIC
FLAT PANEL MATERIAL CHARACTERIZATIONE. MILLS
11/07/90

PROPERTY	ORIENTATION	TEMPERATURE - DEGREES F										
		70	TBD(3)	TBD(3)	TBD(3)	TBD(3)	1200	1500	2000	2500	3500	5000
TENSION(1,5)	WARP	3			3		3		3		3	
	FILL	3			3		3		3	3	3	3
	ACROSS-PLY	3	3	3	3	3	3	3	3	3	3	3
COMPRESSION(1,5)	WARP	3			3		3		3		3	
	FILL	3		3	3		3		3	3	3	3
	ACROSS-PLY	3	3	3	3	3	3	3	3	3	3	3
45 DEG OFF-AXIS		3		3	3		3		3	3	3	3
SHEAR STRENGTH	INTERLAMINAR	3	3	3	3	3	3	3	3	3	3	3
	WARP/FILL	3		3	3		3		3	3	3	3
SHEAR MODULUS	TORSION	3		3	3		3		3	3	3	3
		RT to 1800 DEG F					1800 to 5000 DEG F					
CTE(4)	WARP	3										
	FILL	3										
	(2) ACROSS-PLY 1F/S	3										
(2)	ACROSS-PLY 10F/S	3										
(2)	ACROSS-PLY 30F/S	3										
RTG to 1500F	ACROSS-PLY	3										

NOTES:

- 1 MODULUS, YIELD STRAIN, MAXIMUM STRESS, FAILURE STRAIN, AND POISSON'S RATIO AT 70F
- 2 HEATING RATES: 1, 10, 30 F PER SECOND UP TO 1800F. 1F PER SECOND FROM 1800 TO 5000F
- 3 TBD TEMPERATURES TO BE DETERMINED BASED ON REVIEW OF CTE TEST RESULTS
- 4 CTE TESTS USING QUARTZ DILATOMETER FROM 70F TO 1500/1800F; GRAPHITE DILATOMETER UP TO 5000F
- 5 MODULUS, YIELD STRAIN, MAXIMUM STRESS, FAILURE STRAIN, AT ELEVATED TEMPERATURE

TI2PHEN4.WQ1

E. MILLS

11/07/90

TABLE 2

CSD TITAN 4 - CARBON OR GRAPHITE PHENOLIC
MATERIAL CHARACTERIZATION - VARIABILITY

PROPERTY	ORIENTATION	TEMPERATURE - DEGREES F							
		70	TBD(3)	TBD(3)	TBD(3)	TBD(3)	TBD(3)	1200	
TENSION(1,5)	WARP	3				3		3	
	FILL								
	ACROSS-PLY	3		3		3		3	
COMPRESSION(1,5)	WARP	3				3		3	
	FILL								
	ACROSS-PLY 45 DEG OFF-AXIS	3		3		3		3	
SHEAR STRENGTH	INTERLAMINAR	3		3		3		3	
	WARP/FILL								
	TORSION								
		RT to 1800 DEG F				1800 to 5000 DEG F			
CTE(4)	WARP	3				3			
	FILL	3				3			
	ACROSS-PLY 1F/S	3				3			
(2)	ACROSS-PLY 10F/S	3							
(2)	ACROSS-PLY 30F/S	3							
RTG to 1500F		3							

NOTES:

- 1 MODULUS, YIELD STRAIN, MAXIMUM STRESS, FAILURE STRAIN, AND POISSON'S RATIO AT 70F
- 2 HEATING RATES: 1, 10, 30 F PER SECOND UP TO 1800F. 1F PER SECOND FROM 1800 TO 5000F
- 3 TBD TEMPERATURES TO BE DETERMINED BASED ON REVIEW OF CTE TEST RESULTS
- 4 CTE TESTS USING QUARTZ DILATOMETER FROM 70F TO 1500/1800F; GRAPHITE DILATOMETER UP TO 5000F
- 5 MODULUS, YIELD STRAIN, MAXIMUM STRESS, FAILURE STRAIN, AT ELEVATED TEMPERATURE

TI3PHEN6.WQ1

TABLE 3

CSD TITAN 4 - CARBON OR GRAPHITE PHENOLIC
MATERIAL CHARACTERIZATION - MISCELLANEOUS

E. MILLS
11/07/90

PROPERTY	ORIENTATION	TEMPERATURE	
		70F	70-1000F 70-1200F
MOISTURE CONTENT	--	2	
MOISTURE DIFFUSION	IN-PLANE WARP	2	
RESIN CONTENT	--	2	
TGA	--		2
PLY LIFT	PART-SPECIFIC		3

T14PHEN7.WQ1

E. MILLS

11/09/90

TABLE 4
CSD TITAN 4 - CARBON AND GRAPHITE PHENOLIC
PANEL TEST MATERIALS & SOURCES

TEST MATRIX (DTP-4052-006-)	PREPREG MANUFACTURER (PRESS CURED - NPC) (1)	COPROCESSED TM3 (AUTOCLAVE)	COPROCESSED FULL SCALE (HYDROCLAVE)	TOTAL
TABLE 1	NONE	NONE	1. FM5014-NAR NPC (6)	
CHARACTERIZATION			2. MX4926/VCK-NAR PC	2
TABLE 2	1. FM5014-NAR (2) LOT #1	1. FM5014-NAR NPC	1. FM5014-NAR PANELS PC (6)	
VARIABILITY	2. FM5014-NAR LOT #2	2. FM5014-NAR PC	2. FM5014-NAR EXIT CONE TAG END NPC (5)	
	3. FM5014-NAR LOT #3	3. MX4926/VCK-NAR PC	3. FM5014-NAR THROAT TAG END PC (4)	
	4. MX4926/VCK-NAR LOT #1	4. FM5014-AVTEX NPC	4. MX4926/VCK-NAR A/C INSERT TAG END PC (3)	
	5. MX4926/VCK-NAR LOT #2	5. FM5014-AVTEX PC		
	6. MX4926/VCK-NAR LOT #3	6. MX4926/VCK-AVTEX PC		16
TABLE 3	NONE	NONE	1. FM5014-NAR NPC	
MISCELLANEOUS			2. FM5014-NAR PC	
			3. MX4926/VCK-NAR PC	3

NOTES: 1. NPC = NO POST CURE; PC = POST CURED

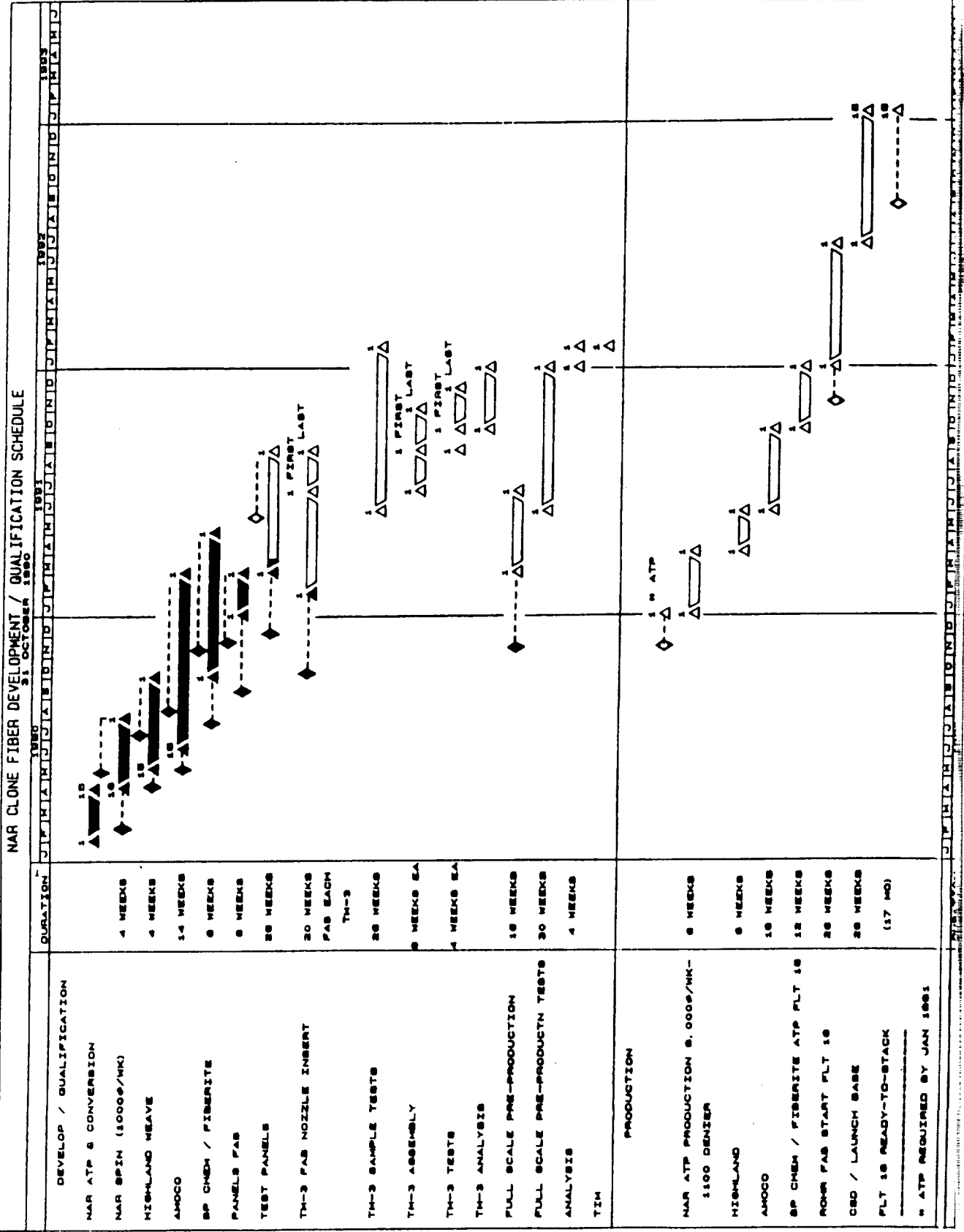
2. NAR = NORTH AMERICAN RAYON #23; AVTEX = AVTEX RESTART RAYON

3. MX4926/VCK AFT CLOSURE INSERT - BIAS TAPE WRAPPED - FREE STANDING POST CURE @310F

4. FM5014 THROAT RINGS - FLATWISE INVOLUTE - FREE STANDING POST CURE @310F MAX

5. FM5014 EXIT CONE - STRAIGHT TAPE WRAPPED PARALLEL TO CL - NO POST CURE

6. FM5014 NPC / PC ENTRIES FROM PREVIOUS (6-90) TABLE 4 CORRECTED HERE



CSD TITAN 4

NARC RAYON QUALIFICATION

WCA GRAPHITE (1100d RAYON) APPLICATIONS

TITAN 4 - FM5014 - GRAPHITE PHENOLIC *
STANDARD MISSILE - FM5014 - GRAPHITE PHENOLIC *
SRMU - GRAPHITE PHENOLIC (?)
D5 IGNITER - GRAPHITE PHENOLIC
IUS - FM5064 - 2D CARBON-CARBON
INTELSAT - FM5064 - 2D CARBON-CARBON
PEACEKEEPER - FM5064 - 2D CARBON-CARBON *
SHUTTLE (MAIN VEHICLE) - 2D CARBON-CARBON
ALGOL - GRAPHITE PHENOLIC
STAR MOTORS (?)

* INDICATES QUALIFICATION EFFORT UNDERWAY

CSD TITAN 4

NARC RAYON QUALIFICATION

CONCLUSIONS:

A SUBSTANTIAL CHARACTERIZATION EFFORT IS UNDERWAY AT CSD FOR TITAN NARC 1100d RAYON BASED CLOTHS - BOTH WCA and VCK.

THE MECHANICAL TESTS ARE CONSISTENT WITH NASA SPIP & USAF PROPOSED CHARACTERIZATION TEST METHODS AND MATRICES.

SOME TEMPERATURES AND PROPERTIES, PARTICULARLY TITAN THERMAL TESTS BEING PERFORMED BY AEROTHERM, ARE NOT CURRENTLY INCLUDED FOR TEST PER THE CSD TABLE 1 MATRIX.

SPARE PANEL MATERIAL WILL BE AVAILABLE FROM CSD TITAN EFFORT

RECOMMENDATIONS:

COORDINATE EXISTING TITAN MATRIX WITH USAF / AEROSPACE TO ADD A SUPPLEMENTAL EFFORT TO COMPLETE THE PROPOSED 1100d NARC CHARACTERIZATION USING RESIDUAL CSD PANEL MATERIAL.

CHARACTERIZATION OF SECOND SOURCE 1100d (OTHER THAN NARC)

APPENDIX G

GLORIA MA

1990 ASNT Fall Conference and Quality Testing Show

NDT for Today's Applications

**Seattle Sheraton and Towers
Seattle, Washington
October 8-12, 1990**



**The American Society for Nondestructive Testing, Inc.
1711 Arlingate Lane
Columbus, OH 43228-0518**

AN INSTRUMENT FOR THE NON-DESTRUCTIVE DETERMINATION OF FIBER/RESIN RATIO IN FIBER-REINFORCED COMPOSITE PREPREG MATERIALS

Bruce Reynolds and Dick Zimmerman
ICI/Fiberite
2055 East Technology Circle, Tempe, Az. 85284

Gloria Ma and Malcolm D. Campbell
The Expert System Technologies (TEST)
4025 Avati Drive, San Diego, Ca. 92117

A Quantitative NDE instrument (URA 2000) capable of determining the fiber/resin ratio of prepregs quickly, accurately and inexpensively, is presented.

Material properties and mechanical behavior of composite materials depend on their fiber and matrix content. Hence, these are held to tight specifications, and the demands for testing are high for aerospace applications. The current industry standards for determination of fiber/resin ratios involve some form of destructive analysis^{1,2,3,4}. This is accomplished by weighing the intact sample, removing the resin by chemical action or combustion, and weighing the remaining fibers. These methods are time-consuming, expensive, hazardous, variable from operator to operator and create toxic wastes. Consequently, there is a strong need for a quick, accurate and inexpensive method for determining fiber/resin ratio that is independent of operator skills.

Contact measurements on prepreg materials present a technical challenge. As a result of the flowable nature of the uncured resin, dynamically unstable conditions are created when these materials are contacted with the sensors during the measurement process. A patented process to standardize reference points, called "optimal consolidation", is necessary to obtain repeatable results in prepreg materials⁵.

The basic assumption of the measurement concept is that ultrasonic velocity, and fiber/resin ratio of composite materials are functions of the modulus and density of the material. Hence, there should be a precise and predictable relationship between ultrasonic velocity and fiber/resin ratio. There are various theoretical models to predict this relationship. However, the URA 2000 utilizes a pragmatic approach. It utilizes empirical knowledge gained from calibration data to minimize errors that might result from a purely theoretical treatment since there could be a deviation from theory for particular specimens, and systematic measurement effects^{6,7}. Statistical techniques are employed to maximize accuracy, and to minimize random errors.

The essence of the technique involves simultaneous determination of thickness, ultrasonic time-of-flight and velocity of the prepreg material under optimal consolidation conditions. These measurements are correlated with destructive resin content to establish a material-specific calibration database which is subsequently used to evaluate unknown samples of the same type nondestructively.

The accuracy and precision of this nondestructive technique, as well as the material-specific calibration database on a wide variety of prepreg materials (Table 1) and parallel testing data from verification experiments (Table 2) will be presented. Potential applications of this technology for process control and design optimization will be discussed.

TABLE 1
MATERIAL-SPECIFIC CALIBRATION DATABASE
GENERATED BY THE URA 2000

<u>Designation</u>	<u>Type</u>	<u>Correlation Coefficient</u>		
		<u>Thickness</u>	<u>TOF</u>	<u>Slowness</u>
MXG 7620/2577	Graphite/Epoxy	.9805	.9900	.8426
HyE 1377-2TB	Graphite/Epoxy	.9821	.9480	.4790
HyE 1534A	GY70/Epoxy	.9789	.9824	.9079
HyE 3034K	T300(12K)/Epoxy	.9856	.9377	.6493
HyE 1034C	T300(3K)/Epoxy	.9263	.8895	.9599
HyE 2134B	T50(3K)/Epoxy	.9921	.9937	.9745
HyE 2034D	Pitch75/Epoxy	.9789	.9825	.7633
MXB 7251/120	Glass/Epoxy	.9976	.9971	.9804
MXB 7669/7781	Glass/Epoxy	.9914	.9958	.9900
MXB 7701/1581	Glass/Epoxy	.9868	.9775	.8452
MXB 7701/7781	Glass/Epoxy	.9942	.9889	.8837
MXB 7701/120	Glass/Epoxy	.9948	.9951	.9703
MXB 7701/1581	Glass Epoxy	.9685	.9893	.9053
MXB 7711/7781	Glass/Epoxy	.9938	.9944	.9873
MXB 7934/120	Glass/Epoxy	.9973	.9969	.9685
MXB 9002/120	Glass/Epoxy	.9996	.9995	.9975
MXB 9002/181	Glass/Epoxy	.9831	.9959	.9547
MXB 9002/7781	Glass/Epoxy	.9981	.9981	.9985
MXB 9022/7781	Glass/Polyester	.9812	.9884	.9527
MXB 6070/5322	Glass/Phenolic	.9969	.9955	.7697
MXB 6032/7781	Glass/Phenolic	.9728	.9817	.9528
MXM 7251/220K	Kevlar/Epoxy	.9995	.9994	.9725
MXM 7880/285K	Kevlar/Epoxy	.9956	.9944	.9121
MXM 7764/285K	Kevlar/Epoxy	.9961	.9974	.9872
MXM 7714/120K	Kevlar/Epoxy	.9979	.9959	.9223
MXM 7714/281K	Kevlar/Epoxy	.9913	.9950	.9575
MXM 7701/52006	Kevlar/Epoxy	.9870	.9743	.5824
MXM 7934/120K	Kevlar/Epoxy	.9871	.9770	.2218
MXM 7934/52006	Kevlar/Epoxy	.9605	.9589	.5596

TABLE 2

SUMMARY OF PARALLEL TESTING DATA AT ICI/FIBERITE (ORANGE)

<u>Material</u>	<u>Type</u>	<u>Batch #</u>	<u>Date</u>	<u>Std. Dev.</u>	<u>Var.</u>	<u>n</u>
MXM 7714/285K	Kev/Ep	H89-6790	1/9/90	0.46	0.21	30
		H90-7874	6/4/90	0.49	0.24	36
		H90-7884	6/7/90	0.29	0.08	27
		H90-7917	6/13/90	0.24	0.06	23
MXB 7701/7781	Gl/Ep	H89-6604	12/06/89	0.58	0.34	39
		H90-7886	6/7/90	0.69	0.48	49
MXM 7714/120K	Kev/Ep	H89-6769	1/10/90	0.81	0.65	39
MXB 7701/120	Gl/Ep	H90-7944	6/14/90	0.35	0.12	28

References

1. ASTM Standard C613: Test Method for Resin Content of Carbon and Graphite Prepregs by Solvent Extraction. ASTM Standards and Literature References for Composite Materials. First Edition, 1987.
2. ASTM Standard D2584: Test Method for Ignition Loss of Cured Reinforced Resin. ASTM Standards and Literature References for Composite Materials. First Edition, 1987.
3. ASTM Standard D3529: Test Method for Resin Solids Content of Carbon Fiber-Epoxy Prepreg. ASTM Standards and Literature References for Composite Materials. First Edition, 1987.
4. Test Method for Resin and Volatile Content of Preimpregnated Inorganic Reinforcements. Society of the Plastics Industry: SPI Prepreg 1 (revised February 1962).
5. U. S. Patent 4,856,335 (Aug. 15, 1989) Method of Establishing Standard Composite Material Properties.
6. U. S. Patent 4,794,545 (Dec. 27, 1988) Nondestructive Measurement of Fractions of Phases in Mixtures and Composite Materials.
7. U. S. Patent 4,897,796 (Jan. 30, 1990) Nondestructive Measurement of Fractions of Phases in Mixtures and Composite Materials.

APPENDIX H
MAJOR STEVE OPEL

2

**BRIEFING TO JANNAF ON
PROPOSED JOINT AIR FORCE/NASA ALTERNATE SOURCE
RAYON CHARACTERIZATION PLAN (1650 DENIER)**

OVERVIEW

**PRESENTED BY: CAPT PAT FILLINGIM, USAF
CHIEF, GROUND SYSTEMS ENGINEERING
USAF SPACE SYSTEMS DIVISION**

RAYON BRIEFING OUTLINE

- REVIEW
 - CONCEPT
 - RATIONALE
 - FLOW
- INDUSTRY RESPONSE REVIEW
- REVISED CONCEPT
- CRITERIA FOR 2ND SOURCE SELECTION
- ANNOUNCEMENT DATE OF 2ND SOURCE
- TIMELINE

PURPOSE OF BRIEFINGS

- OPEN FORUM TO INFORM INDUSTRY OF PROPOSED EFFORT
- SEEK COMMENTS FROM INDUSTRY ON PROGRAM
 - UTILITY
 - VALIDITY
 - TEST MATRIX CONTENTS, ETC
- DIRECT INDUSTRY TO INTEGRATE THIS PLANNED EFFORT INTO THEIR PROPOSAL OR PLANNED ACTIVITIES
- PROVIDE INFORMATION ON GOVERNMENT TEST FACILITIES
- INCORPORATE INDUSTRY COMMENTS INTO FINAL PLAN TO BE PRESENTED AT JANNAF CONFERENCE AT JPL

CHRONOLOGY OF AEROSPACE RAYON YARNS

AEROSPACE RAYON YARNS HAVE BEEN DOMESTICALLY PRODUCED SINCE THE 1960s

Y E A R

E V E N T

1940

COURTAULDS OPEN FRONT ROYAL, VA PLANT

1964

IRC-AMERICAN CYANAMID PRODUCES FIRST AEROSPACE GRADE RAYON YARNS

1972

AMERICAN ENKA PRODUCES AEROSPACE RAYON YARNS

1976

AMERICAN VISCOSE-FMC PRODUCES AEROSPACE RAYON YARNS

1976

AVTEX FIBERS, INC. PURCHASES FMC FRONT ROYAL, VA PLANT AND CONTINUES AEROSPACE RAYON PRODUCTION

1988

AVTEX FIBERS, INC. CLOSES FRONT ROYAL PLANT

1988

DOD AND NASA PROVIDE \$44M TO RE-OPEN AVTEX FRONT ROYAL PLANT

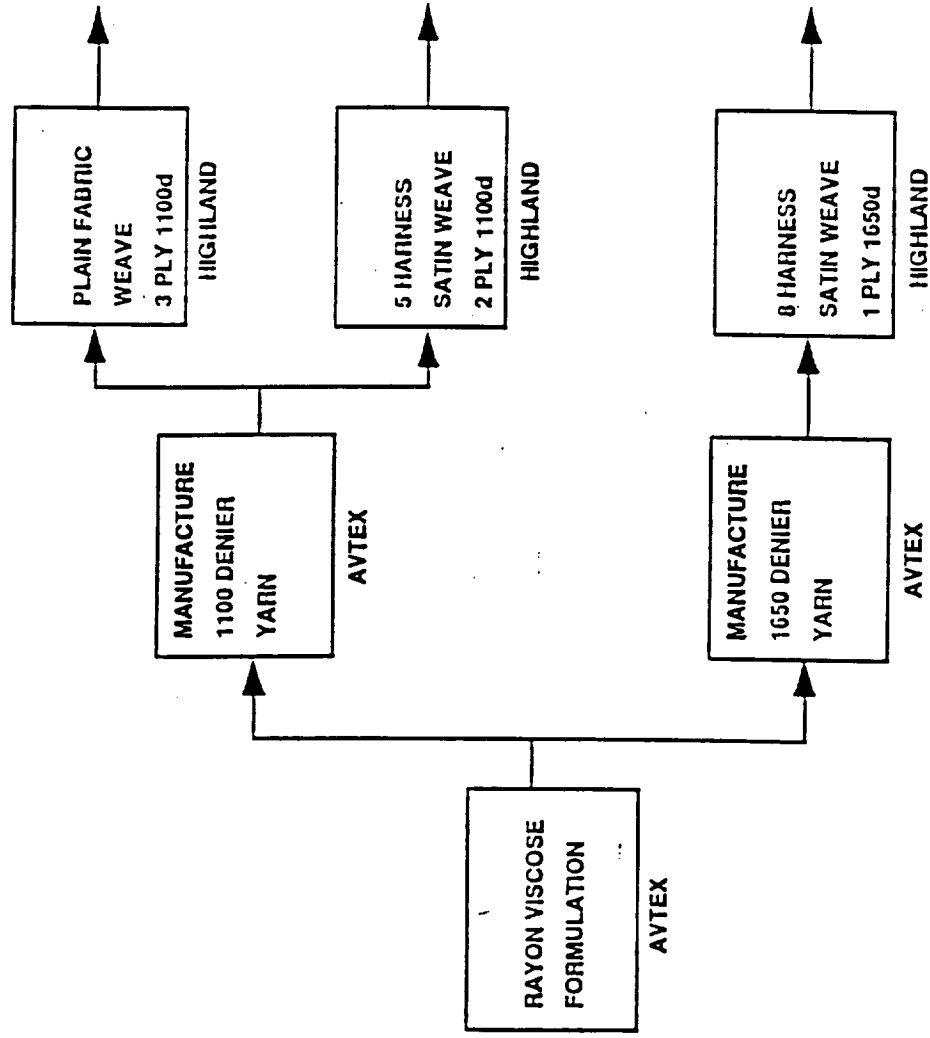
1988

NASA STARTS DEVELOPMENT OF SECOND SOURCE (NORTH AMERICAN)

1989

AVTEX FIBERS, INC. CLOSES FRONT ROYAL PLANT

BASELINE AVTEX FABRIC PRODUCTS



Structural Mechanics Subdivision
Vehicle and Control Systems Division
THE AEROSPACE CORPORATION

U.S. ORGANIZATIONS IMPACTED

- BOTH GOVERNMENT AND COMMERCIAL ORGANIZATIONS ARE IMPACTED
 - DEPARTMENT OF DEFENSE
 - STRATEGIC SYSTEMS
 - TACTICAL SYSTEMS
 - SPACE SYSTEMS
- NASA
 - GROUND LAUNCH SYSTEMS (SHUTTLE)
 - SPACE SYSTEMS
- COMMERCIAL
 - GROUND LAUNCH SYSTEMS
 - SPACE SYSTEMS

IMPACTED AEROSPACE INDUSTRIES

o FIVE LEVELS OF AEROSPACE INDUSTRIES WOULD BE IMPACTED

PRIME SYSTEMS MANUFACTURERS

- o MORTON THIOKOL, INC.
- o HERCULES, INC.
- o UTC/CHEMICAL SYSTEMS DIV.
- o AEROJET STRATEGIC PROPULSION CO.
- o ATLANTIC RESEARCH CORP.
- o LOCKHEED MISSILES & SPACE CO.
- o MCDONNELL DOUGLAS CORP.
- o AVCO CORP.
- o GENERAL ELECTRIC CO.
- o MARTIN MARIETTA CORP.
- o BOEING AEROSPACE
- o GENERAL DYNAMICS
- o ROCKWELL

PRIME COMPONENT MANUFACTURERS

- o MORTON THIOKOL, INC.
- o HITCO MATERIALS DIV.
- o HERCULES, INC.
- o UTC/CHEMICAL SYSTEMS DIVISION
- o REINHOLD INDUSTRIES, INC.
- o KAISER AEROTECH
- o ROHR INDUSTRIES, INC.
- o AEROJET STRATEGIC PROPULSION CO.
- o EDLER INDUSTRIES, INC.
- o LTV AEROSPACE & DEFENSE
- o AMERICAN AUTOMATED ENGINEERING, INC.

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IMPACTED AEROSPACE INDUSTRIES (CONTINUED)

PREPREG MANUFACTURERS

- FIBERITE
- U.S. POLYMERIC

FABRIC WEAVER

- HIGHLAND INDUSTRIES
- MILLIKEN

CARBON YARN CONVERTERS

- AMOCO PERFORMANCE PRODUCTS, INC.
- HITCO MATERIALS DIVISION
- POLYCARBON, INC.

RAYON USAGE

Program	Amount of Rayon Per Mission (Klbs)				Use/Production Per Year	Total Rayon Requirement Per Year (Klbs)		
	1650dr (8HS)	1100dr (5HS)	1100dr (PW)	Total		1650dr (8HS)	1100dr (5HS)	1100dr (PW)
Titan IV	0	10	20	30	4 - 7	40 - 70	50 - 88	30 - 53
Titan SRMU	27	-	7	34	4 - 8	108 - 216	-	28 - 56
Della II*	9.2	-	-	9.2	8 - 12	74 - 110	-	-
IUS	1.2	-	9(C-C)	10.2	4 - 6	5 - 7	-	36 - 54
MX†	10.1	-	4(C-C)	14.1	7 - 13	71 - 131	-	28 - 52
Shuttle SRM	100	-	-	100	8 - 12	800 - 1200	-	-
Navy D5**	-	-	-	-	-	480 - 525	-	-
Navy Standard Missile	0.1	-	0.06	0.16	800 - 1000	80 - 100	-	48 - 60

* Includes Star 48

† Excludes RV

** Includes RV Heat Shields

MAXIMUM

TOTALS ----- **2359** **88** **275**

VULNERABILITY

- SINGLE SOURCE (YET TO BE QUALIFIED)
- STOCKPILE OF OLD MATERIAL NON-EXISTENT ABOVE PROGRAM OFFICE-LEVEL
- ALTERNATE/NEXT GENERATION MATERIALS (PAN) NOT READY
- UNABLE TO MEET SURGE REQUIREMENTS
- UNCERTAINTY OF REGULATORY REQUIREMENTS (EPA/OSHA) IN THE FUTURE

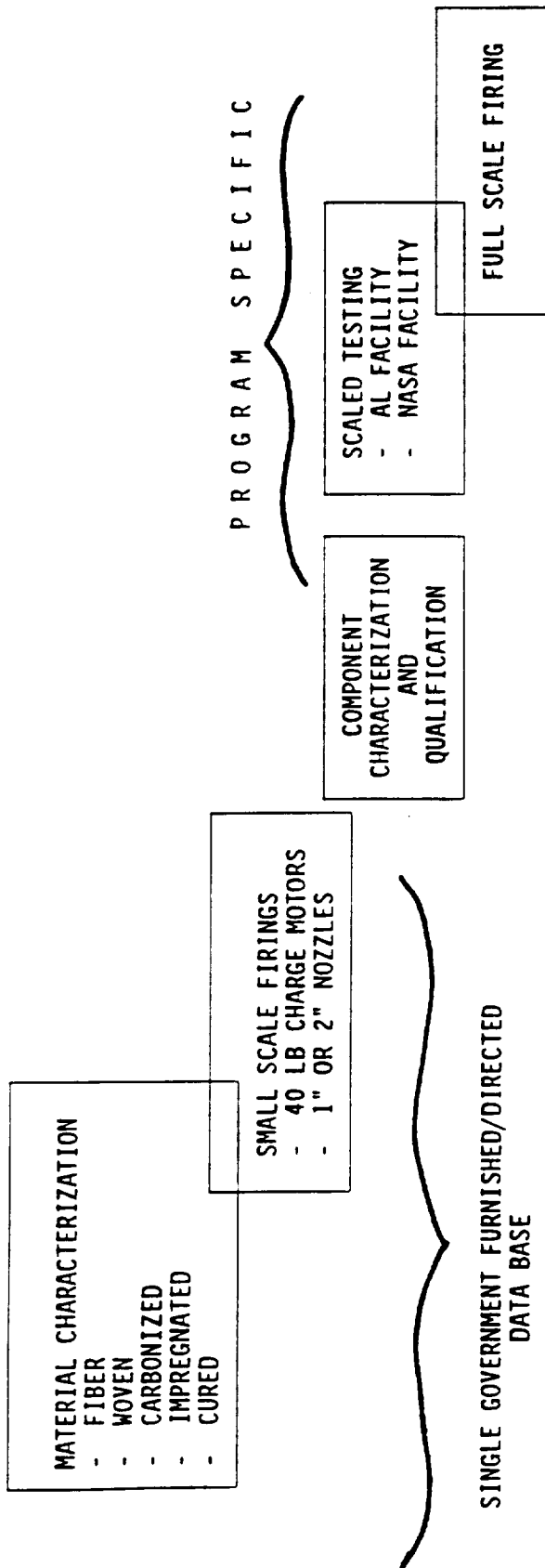
COST

- HISTORICAL TREND:

Y E A R	P R I C E
1971	0.78
1972	1.08
1976	1.63
1988	3.81 (PRE-SHUTDOWN)
1988	6.98 (POST-SHUTDOWN)
1989	5.60
1990	5.65
199X	?

- ALWAYS BEEN IN SOLE SOURCE ENVIRONMENT
- MAGNITUDE AT TOTAL GOVERNMENT LEVEL
\$1.00 INCREASE AT RAYON FIBER LEVEL -- \$2.5M/YEAR

PROPOSED EFFORT



RAYON CHARACTERIZATION APPROACH

RAYON FIBERS FROM AVTEX, NARC, AND ALTERNATE SOURCE
- 8 HARNESS SATIN WEAVE, 1650 DENIER, LOW FIRED (1350 C)

RAYON FIBERS FROM NARC

- PLAIN WEAVE, 1100 DENIER, HIGH FIRED (1600 C)

MATERIAL PROPERTY TESTS

- RAYON FIBER
- WOVEN FABRIC
- CARBONIZED FABRIC
- IMPREGNATED FABRIC (UNCURED)
- CURED COMPOSITE

SUBSCALE STATIC FIRING TESTS

PROGRAM SPECIFIC TESTS

- LONG DURATION SUBSCALE STATIC TESTS
- EXTENSIVE COMPONENT CHARACTERIZATION TESTS
- FULL-SCALE STATIC FIRING TESTS

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INDUSTRY RESPONSE TO 16 AUGUST 1990 BRIEFING

o TWENTY FIVE ORGANIZATIONS IN ATTENDANCE

oo Rayon Fiber Source
oo Weave Source
oo Carbon Fabric Source
oo Prepreg Source
oo Composite Fabricator
oo Composite User
oo Government Sponsor

o SIXTEEN ORGANIZATIONS RESPONDED WITH INPUT, OPINIONS OR REQUESTS (19 OCTOBER)

ACTION DUE TO INDUSTRY RESPONSE

- MOISTURE DIFFUSION AND MICROSTRUCTURE OF COMPOSITE
- CERTIFY/DEFINE RESINS AND FILLERS
- TIMELY DISSEMINATION OF DATA (INTERIM MEETING & PUBLISHED DATABASE)
- SIMULATE HARDWARE PROCESSING DURING FLAT PANEL FABRICATION

COMPOSITE MATERIAL CHARACTERIZATION PLAN (1) - (4)

PROPERTY	ORIENTATION	TEMPERATURE, °F													
		70	250	350	400	500	600	750	900	1200	1500	2000	3500	4500	
TENSION	WARP FILL ACROSS-PLY 45°	5		5		5		5	5			5	5		
		10	5	5		5	5	5	5	5		5	5		
		10	5	5	5	5	5	5	5	5	5		5	5	
		5		5		5		5				5	5		
COMPRESSION	WARP FILL ACROSS-PLY 45°	5		5		5						5		5	
		5		5		5		5		5		5		5	
		5	5	5	5	5	5	5	5	5		5	5	5	
		5		5		5							5		
SHEAR STRENGTH	INTERLAMINAR WARP/FILL	10						5							
	5		5				5	5	5		5	5	5		
SHEAR	INTERLAMINAR	5	5	5		5		5	5	5	5	5	5	5	
		3,3,3(5)									3			▲	
		3,3,3(5)									3			▲	
		6,6,10(6)									3			▲	
RTG	ACROSS PLY	6,6,10(6)													
										▲					
EMISSION		3													
PERMEABILITY	ACROSS-PLY, FILL	3,3								▲					
THERMAL CONDUCTIVITY	WARP/FILL	3,3												▲	
	ACROSS-PLY	3												▲	
TGA	---	4													
										▲					
SPECIFIC HEAT	---	3												▲	

- (1) TEST PLAN FOR GRAPHITE PHENOLIC (1100 DENIER) AND CARBON PHENOLIC (1650 DENIER) COMPOSITES.
- (2) FLAT PANELS MADE WITH AVTEX, NARC AND ALTERNATE RAYON FIBERS.
- (3) NDI FOR TEST SPECIMENS, AS APPROPRIATE.
- (4) CHARACTERIZATION FOR MOISTURE DIFFUSION, VOLATILE CONTENT, MAX MOISTURE CONTENT AND MICROSTRUCTURE.
- (5) THREE SPECIMENS AT 1,10,50 °F/SEC EACH, PLUS FIVE SPECIMENS AT 50 °F/SEC. TWO SPECIMEN GEOMETRIES FOR EACH SET.
- (6) THREE SPECIMENS AT DRY AND WET CONDITIONS, 10 °F/SEC EACH.

10/25/90



REVISED CONCEPT

1. 1650d SECOND SOURCE CHARACTERIZATION

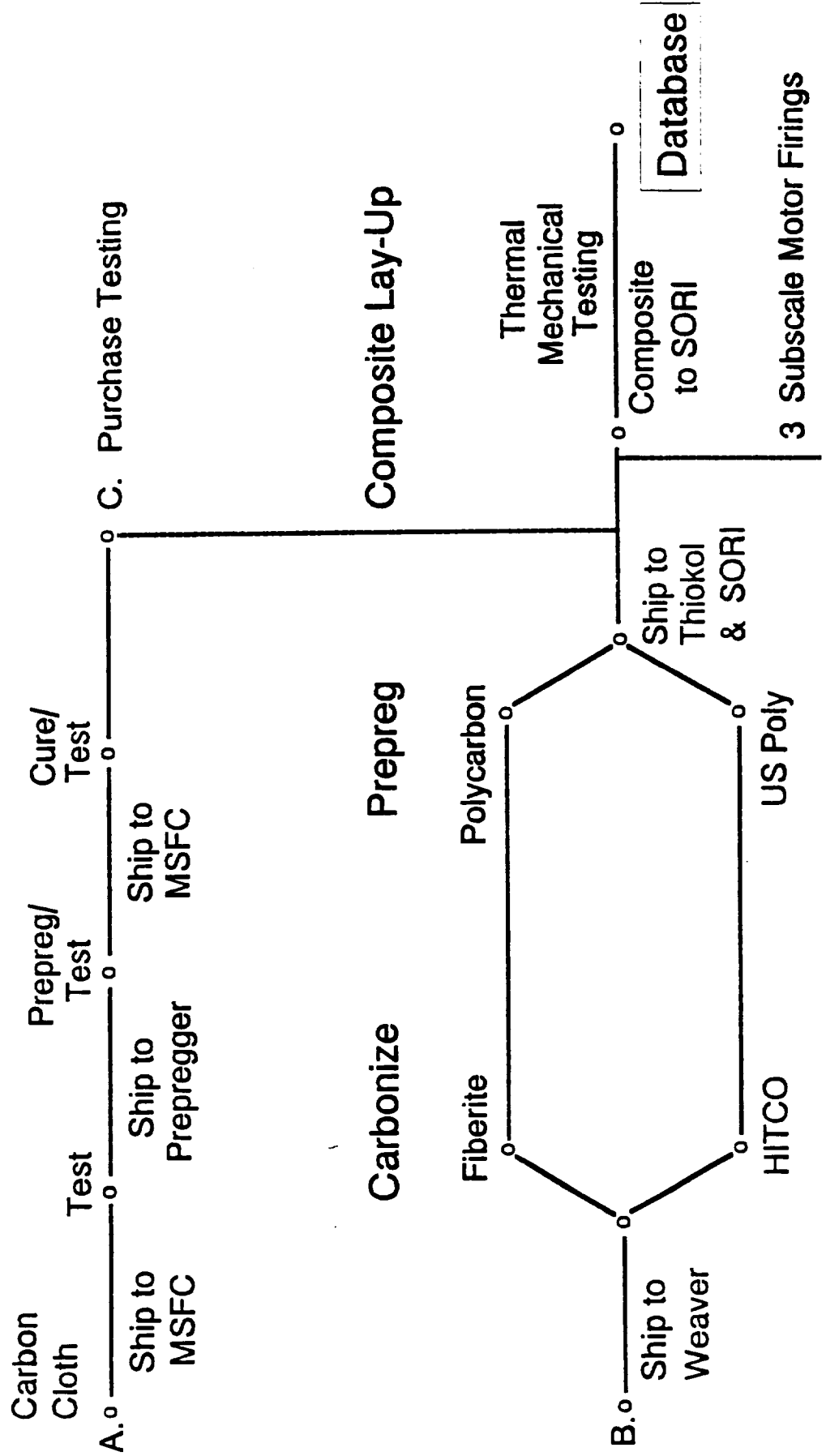
- A. PURCHASE 50 LBS OF CARBON CLOTH FABRICATED TO NASA SHUTTLE SPECIFICATION - DELIVERABLE NLT 30 DAYS AFTER CONTRACT AWARD
- B. PURCHASE MATERIAL WITH REQUIRED TESTING, SPEC'S AND PROCESS DOCUMENTATION FOR OPERATIONS UP TO PRODUCIBILITY/COMPOSITE LAY-UP AND T/M TESTING
- C. PURCHASE REMAINDER OF PROGRAM - TESTING/ PRODUCIBILITY/ DEMO/ETC

PURCHASE "A" & "B" WILL BE MADE FIRST THROUGH SORI TASK ORDER CONTRACT AT BMO

PURCHASE "C" WILL BE MADE FOLLOWING SUCCESSFUL TESTING OF MATERIAL PURCHASED IN "A" ABOVE

Material Flow

(1650 Denier)



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REVISED CONCEPT (CONTINUED)

2. 1100d PRIMARY SOURCE CHARACTERIZATION

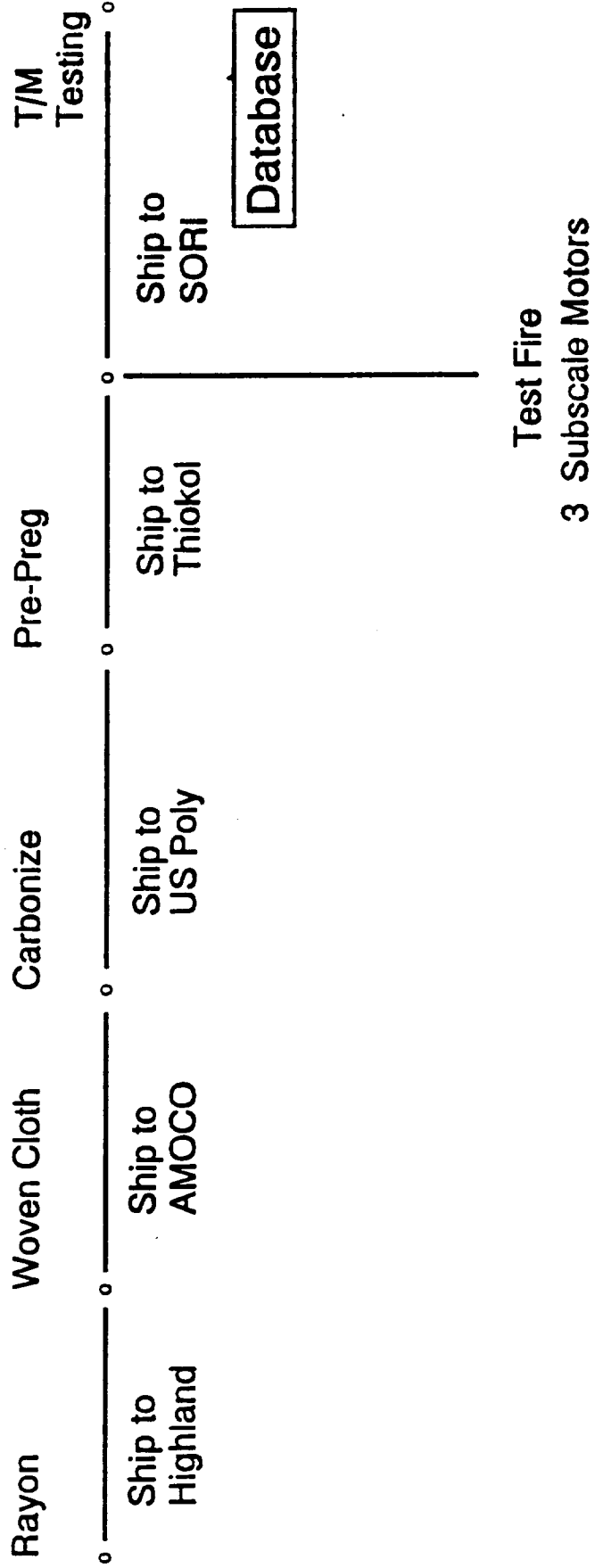
A. PURCHASE TOTAL AMOUNT OF MATERIAL REQUIRED FROM NARC
AND ASSOCIATED TESTING THROUGH SORI TASK ORDER
CONTRACT AT BMO

B. NO 2ND SOURCE FOR 1100d!!

Material Flow

(1100 Denier)

- a. Producibility Demo
- b. Composite Lay-Up
- c. 3 Subscale Motors



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CRITERIA FOR 2ND SOURCE SELECTION

- A. DOMESTIC PRODUCER
- B. DEMONSTRATED CARBONIZABLE PRODUCT
- C. MARKET ACCESSIBILITY
- D. US NOT ONLY CUSTOMER OF PRODUCT
- E. COST
- F. LONG-TERM VIABILITY OF PRODUCTION LINE

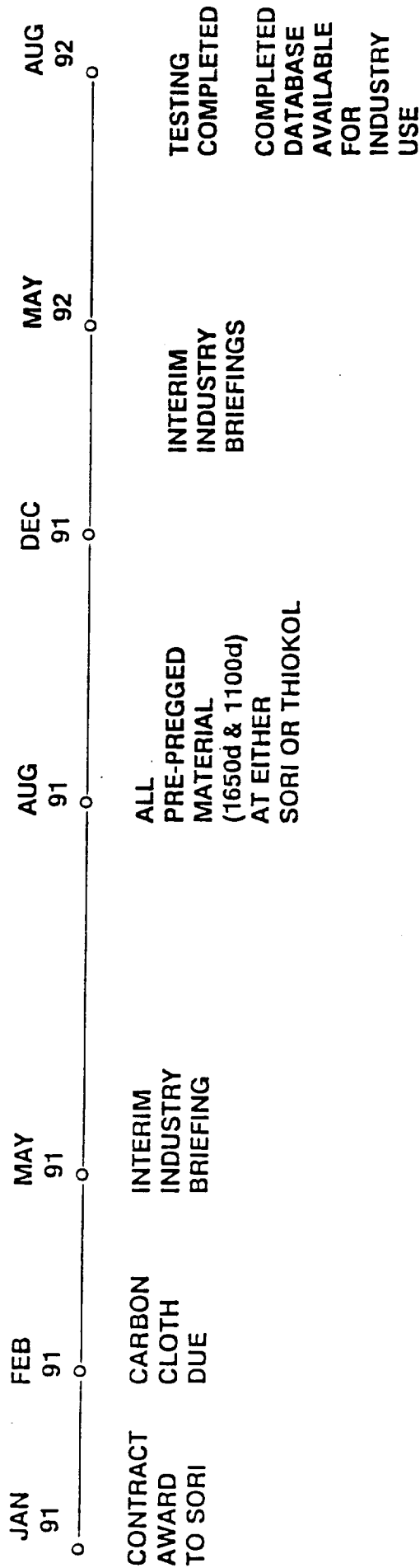
SOURCE OF DATA:

1. NASA REQUEST FOR SOURCES THROUGH THIOKOL
2. PRESENTATIONS TO GOVT (POTENTIAL)

SELECTION METHODOLOGY

- JOINT DECISION
 - MEMBERS FROM:
 - NASA
 - SSD
 - BMO
- MEET 7TH DECEMBER AT MSFC
- DECISION ANNOUNCED VIA TELEPHONE 10TH DECEMBER
- INDUSTRY NOTICE TO BE ISSUED BY 14TH DECEMBER

TIMELINE



- APPROXIMATELY 20 MONTHS IN DURATION
- TIMELINE IS TENTATIVE UNTIL SCHEDULE CAN BE WORKED WITH SORI

CHARACTERIZATION TEST MATRICES AND PROPOSED MATERIAL FLOW

OCTOBER 25, 1990

BY:

BEN NEIGHBORS
PHONE: (205) 544-4986

Presented by A.J. Day

EE53
MSFC, AL. 35812
205-722-4926

APPENDIX I

BOB LOONEY

SOLID PROPULSION INTEGRITY PROGRAM SUBCOMMITTEE

Friday, November 16, 1990

North American Rayon Corp.
Elizabethton, Tennessee 37643

FACTS ABOUT NAR

Established in 1928; the largest single employer in Elizabethton and Carter County, Tennessee.

Employs 1,500 workers with an annual payroll of \$25 million.

Pays approximately \$500,000 in state and local taxes.

Is one of 9,000 employee-owned companies in the United States; and the first employee-owned company in Elizabethton, Tennessee.

Is one of the few ESOP companies where employees own 100 percent of the stock.

Has an annual economic impact of \$45 million locally, including payroll and taxes.

Produces 35 million pounds of rayon annually.

NAR products, including plastic coated fabric and polyester staple, are sold domestically and internationally.

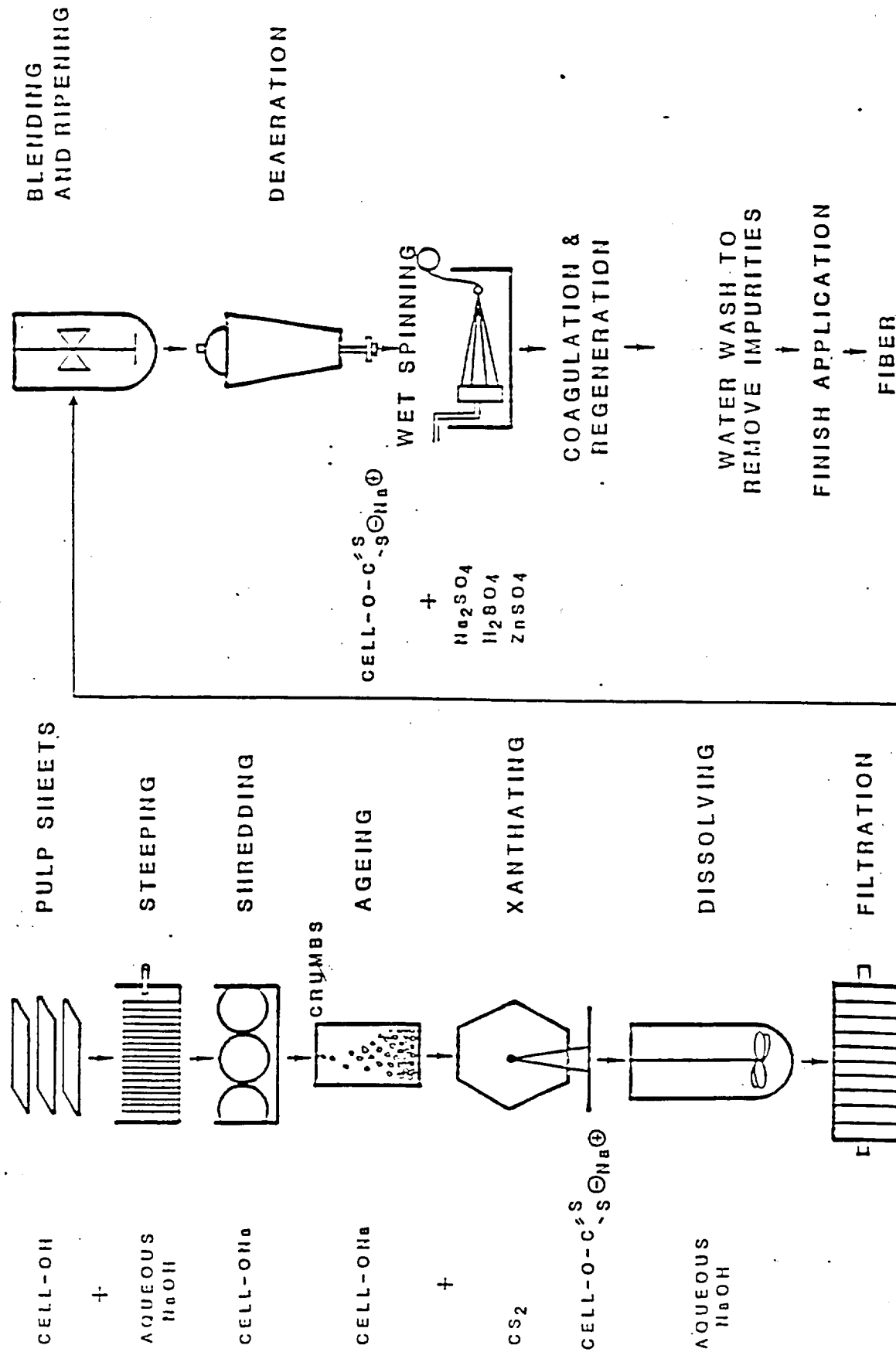
Produces 25 tons of sodium sulfate each day as a by-product which is sold for use in other industries.

The powerhouse produces 274,000 kilowatts of electricity daily for an annual production of 100 million kilowatts.

Water returned to Watauga River is processed through our water treatment plant and is actually cleaner than it was before we used it.

Pays \$2.2 million annually to operate and maintain environmental controls.

VISCOSE RAYON PROCESS



SECOND SOURCE CARBONIZABLE RAYON

CURRENT REQUIREMENTS

<u>PARAMETER</u>	<u>1650 DENIER</u>	<u>1100 DENIER</u>
BREAK STRENGTH (LBS)	10.3 - 13.5	7.0 - 9.6
ELONGATION (%)	5.5 - 9.5	5.4 - 9.4
SHRINKAGE (%)	2.9 - 4.7	2.6 - 4.6
MOISTURE (%)	13.0 MAX	13.0 MAX
ASH (%)	0.45 MAX	0.45 MAX
SULFUR (%)	0.25 MAX	0.25 MAX
ZINC (%)	0.07 MAX	0.07 MAX
pH	5.0 - 8.0	5.0 - 8.0
DENIER (GMS/9000 M)	1590 - 1710	1060 - 1140
TWIST (TURNS/INCH)	1.6 -2.4	1.4 -2.2
FINISH (%)	0.2 -1.0	0.2 -1.0

The bitter taste left from the Avtex experience is understandable. Perhaps, the resulting fears can be mitigated if the differences between Avtex and NAR are pointed out; why Avtex failed and NAR is healthy and thriving. Recognizing the significant differences between them should give confidence in NAR's being a long-term supplier:

Avtex was born as a highly leveraged buy-out. NAR does not have the debt service that plagued Avtex.

The bulk of the Avtex production was rayon staple, which competed with cotton and suffered from suppressed prices, resulting in a very low profit margin. Consequently, there was little money for expensive upkeep.

NAR is the only domestic supplier of fine denier textile filament yarn and enjoys excellent diversified business in such markets as women's apparel in woven flat goods and quality woven velvets, knitted lace and woven linings. The yarns are also used for high quality woven and non-woven ribbons. Embroidery yarns are produced from these products, also. Prices for textile yarns are three (3) to four (4) times the price of rayon staple products.

Avtex produced massive quantities (200 million pounds per year) requiring massive quantities of chemicals which require disposition after use.

NAR produces 35 million pounds per year, all continuous filament.

Essentially, Avtex was controlled by one individual. NAR, as an Employee-Owned company, has a stability of commitment and purpose that is in contrast to many individually owned companies.

- NAR has kept pace with and even exceeded environmental standards.

New additions and modifications to the waste water treatment facility were made in 1986.

Personnel were added to the waste treatment facility to provide increased monitoring.

Laboratory testing capabilities were added.

- Monitoring wells were added to the site at strategic spots to increase monitoring.

Water conservation projects reduced hydraulic load by 300,000 gallons per day.

A second clarifier is being added that will increase wastewater settling capacity by 105%, far exceeding acceptable safety margins.

Unlike Avtex, NAR treats all of its viscose waste, thereby avoiding having viscose waste basins and any associated potential problems. In another twelve (12) months NAR will have a sludge dewatering system in place that will eliminate the use of sludge lagoons, enabling NAR to operate without any holding basins.

Confirmation of the environmental protection job that NAR is doing is in the recognition by "Trout Unlimited" in their award to NAR in June, 1989 for efforts the company has made in providing a clean river environment for brown trout and rainbow trout.

Further evidence of NAR's being a good corporate citizen and neighbor is in a portion of the Watauga River DOWN STREAM from NAR having been designated a "TROPHY TROUT STREAM".

NAR is so confident of its environmental performance that it sponsors an annual trout fishing contest which is held on the Watauga River at the plant outfalls!

NASA and the Navy participated in the facilitization costs of the first six spinning machines, but NAR has taken it upon itself to obtain the financial backing for additional equipment, and is currently able to supply all of the program requirements for DoD and NASA (2.0 - 2.7 million pounds per year), and are capable of greater than three (3) million pound capacity with additional capital expenditure.

Therefore, NAR encourages the stockpile approach as the best way to minimize single source risk. Our reasoning includes these considerations:

NAR has the ability to stockpile

Tax money spent on tangible goods rather than on testing costs is more palatable to Congress.

Potential costs and liabilities in having two rayons segregated (for traceability) throughout each company in the chain (weaver, carbonizer, pre-pregger, fabricator, primary contractor) could be significant.

Implications of going away from a U.S.A. tax-paying corporation and its tax-paying employees would be unattractive to Congress.

The inefficiency of dividing a small market between two suppliers could result in a higher price.

In summary, NAR believes that in view of the costs involved for characterization and qualification, the stockpile approach is the prudent resolution to risk minimalization. We know that we are capable.

Some considerations for potential
long term development include:

a) Water soluble finish

NAR can supply sample quantities as well as large quantities of yarn with finishes that would not require dry cleaning solvents that result in hydrocarbon emissions.

b) Yield improvement savings

NAR would be willing to share in yield improvement which could result from expanded specification limits.

c) Carbon loading trials

NAR has the capability of supplying yarn injected with ingredients that could increase carbon yield.